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(54) **Constrained geometry addition polymerization catalysts, processes for their preparation, precursors therefor, methods of use, and novel polymers formed therewith**

Additionspolymerisationskatalysatoren mit eingeschränkter Geometrie, Verfahren zur Herstellung davon, Vorläufer dafür, Verfahren zur Verwendung und daraus hergestellte Polymere

Catalyseurs de polymérisation d'addition à géométrie restreinte, leur procédé de préparation, les précurseurs, procédés d'utilisation et polymères obtenus

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- "Gmelins Handbuch der anorganischen Chemie", vol. 10: "Zirkonium-Organische Verbindungen", vol. 11: "Hafnium-Organische Verbindungen", 1973, Verlag Chemie, GmbH, Weinheim, DE
- CHEMISCHE BERICHTE, vol. 123, no. 8, August 1990, pages 1649-1651, Weinheim, DE; J. OKUDA: "Synthesis and complexation of linked cyclopentadienyl-amido ligands"

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Description

The present invention relates to metal coordination complexes. The invention also relates to certain novel addition polymerization catalysts comprising such metal complexes. Furthermore, the invention relates to methods for the polymerization of addition polymerizable monomers and to the resulting polymers.

Because of the exposure of the active metal site of the metal coordination complexes of the invention, catalysts resulting therefrom have unique properties. Under certain conditions, the catalysts of the invention are capable of preparing novel olefin polymers having previously unknown properties due to their unique facile abilities to polymerize α -olefins, diolefins, hindered vinylidene aliphatic monomers, vinylidene aromatic monomers and mixtures thereof.

Numerous metal coordination complexes are known in the art including such complexes involving monocyclopentadienyl groups and substituted monocyclopentadienyl groups. The present metal coordination complexes differ from those previously known in the art due to the fact that the metal is bound to a cyclopentadienyl or substituted cyclopentadienyl or similar group by both a η^5 -bond and a bridging linkage including other ligands of the metal.

Also previously known in the art are transition metal coordination complexes known as tuckered complexes. Such complexes are described in *Organometallics* 6, 232-241 (1987).

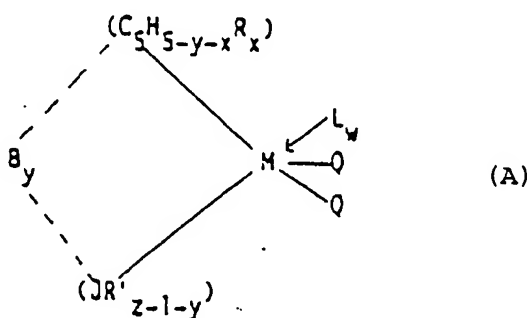
In US Serial No. 8,800, filed January 30, 1987 (published in equivalent form as EP-A-0277004) there are disclosed certain bis(cyclopentadienyl) metal compounds formed by reacting a bis(cyclopentadienyl) metal complex with salts of Bronsted acids containing a noncoordinating compatible anion. The reference discloses the fact that such complexes are usefully employed as catalysts in the polymerization of olefins. The foregoing catalysts are not considered to be particularly effective olefin polymerization catalysts.

Previous attempts to prepare copolymers of vinylidene aromatic monomers and α -olefins, in particular copolymers of styrene and ethylene, have either failed to obtain substantial incorporation of the vinylidene aromatic monomer or else have achieved polymers of low molecular weight. In Polymer Bulletin, 20, 237-241 (1988) there is disclosed a random copolymer of styrene and ethylene containing 1 mole percent styrene incorporated therein. The reported polymer yield was 8.3×10^{-4} grams of polymer per micromole titanium employed.

Thomas K  kenh  hner disclosed, in a thesis entitled "Untersuchungen zur Darstellung Chiraler Organotitan (IV) Verbindung f  r Enantioselektive Synthesen" submitted in August 1983 to Fachbereich Chemie der Philipps-Universit  t Marburg, 1-oxy-3-cyclopentadienyl-propane-1,3-diyl titanium (IV) complexes in which the propanediyl moiety is optionally substituted with alkyl. The exemplified complexes are 1-oxy-1-tert. butyl-3-dimethyl-3-cyclopentadienyl-propane-1,3-diyl titanium dihalides, dimethyl and halide methyl. No use is specified for the complexes.

J. Okuda (Chem. Ber. 123 (1990) 1649-1651; published August 1990) discloses (tert. butylamido)(dimethyl)(3-tert. butyl-cyclopentadienyl) silane titanium dichloride. No use of the complex is specified.

EP-A-0420436 discloses inter alia metal coordination complexes of the Formula A:



wherein:

M is titanium, zirconium or hafnium and is in its highest formal oxidation state (+4, d^0 complex);

$(C_5H_{5-y-x}R_x)$ is (i) a cyclopentadienyl ring which is substituted with from zero to five substituent groups R, x is 0, 1, 2, 3, 4 or 5 denoting the degree of substitution, and each substituent group R is, independently, a C_1 - C_{20} hydrocarbyl radical, a substituted C_1 - C_{20} hydrocarbyl radical wherein one or more hydrogen atoms is replaced by a halogen atom, C_1 - C_{20} hydrocarbyl-substituted metalloid radical wherein the metalloid is of Group 14 of the periodic Table of the Elements, or a halogen atom or (ii) a cyclopentadienyl ring in which two adjacent R-groups are joined forming a C_4 - C_{20} ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

(JR'_{z-1-y}) is a heteroatom ligand in which J is an element with a coordination number of three from Group 15 or an element with a coordination number of two from Group 16 of the Periodic Table of the Elements, and each R' is, independently a C₁-C₂₀ hydrocarbyl radical or a substituted C₁-C₂₀ hydrocarbyl radical wherein one or more hydrogen atoms is replaced by a halogen atom, and z is the coordination number of the element J;

each Q is independently a univalent anionic ligand, provided that where any Q is a hydrocarbyl such Q is different from (C₅H_{5-y-x}R_x), or both Q together are a divalent anionic chelating agent;

B is a covalent bridging group containing an element of Group 14 or 15 of the Periodic Table of the Elements;

L is (i) a Lewis base or (ii) a second transition metal compound of the same type such that the two metal centers M and M' are bridged by Q and Q', wherein M' has the same meaning as M and Q' has the same meaning as Q;

w is a number from 0 to 1; and

y is 0 or 1 when w is greater than 0 and y is 1 when w is 0.

Said metal coordination complexes of EP-A-0420436 are for use with an aluminoxane as a catalyst for olefin polymerization.

EP-A-0418044 (published 20th March 1991) discloses inter alia catalysts corresponding to the Formula B: -



wherein:

Cp is a single η^5 -cyclopentadienyl or η^5 -substituted cyclopentadienyl group optionally covalently bound to M through a substituent;

M is hafnium, titanium or zirconium bound in an η^5 bonded mode to the cyclopentadienyl or substituted cyclopentadienyl group;

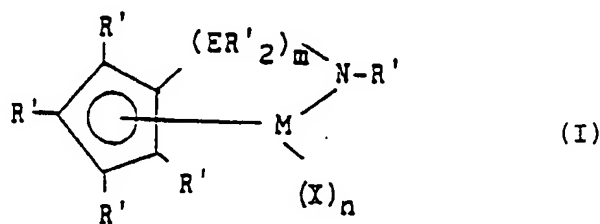
X is independently each occurrence hydride or a moiety selected from halo, alkyl, aryl, silyl, germlyl, aryloxy, alkoxy, amide, siloxy and combinations thereof having of up to 20 non-hydrogen atoms, and neutral Lewis base ligands having up to 20 non-hydrogen atoms or optionally one X together with Cp forms a metallocycle with M of up to 20 non-hydrogen atoms;

R is alkyl or aryl of up to 10 carbons;

n is 1 or 2 depending on the valence of M; and

A⁻ is a noncoordinating, compatible anion of a Bronsted acid salt.

The present invention provides metal coordination complexes of the Formula I:



wherein:

M is titanium bound in an η^5 bonding mode to the cyclopentadienyl group;

R' each occurrence is hydrogen or a moiety selected from silyl, alkyl, aryl and combinations thereof having up to 10 carbon or silicon atoms;

E is silicon;

X each occurrence is halo, alkyl, aryl, or alkoxy of up to 10 carbons;

m is 1 or 2; and

n is 1 or 2 depending on the valence of M.

It should be noted that the complex may exist as a dimer or higher oligomer.

The metal coordination complexes of Formula I can be prepared by contacting a metal compound of the formula MX_{n+2} or a coordinated adduct thereof with a dianionic salt compound corresponding to the Formula II or III:



or



wherein:

L is a metal of Group 1 or 2 of the Periodic Table of the Elements,

Cp^* is the cyclopentadienyl or substituted cyclopentadienyl group $C_5R'_4$ of Formula I,

X^* is fluoro, chloro, bromo, or iodo,

x and y are either 1 or 2 and the product of x and y equals 2, and

n, E, M, m, R' and X are as previously defined

in an inert solvent.

The metal coordination complexes of Formula I also can be prepared by the steps of:

A) contacting a metal compound of the formula MX_{n+1} or a coordinated adduct thereof with a dianionic salt compound corresponding to Formula II or III in an inert solvent; and

B) oxidizing the metal to a higher oxidation state by contacting the reaction product of step A) with a noninterfering oxidizing agent.

The metal coordination complexes of the invention are used with an activating cocatalyst as catalysts in addition polymerizations.

Use of the catalysts can provide EIPE polymers which are highly elastic, interpolymers of ethylene and one or more olefins other than ethylene.

Further, use of the catalysts can provide pseudo-random interpolymers of an α -olefin, particularly ethylene and a vinylidene aromatic monomer, a hindered aliphatic vinylidene monomer, or a mixture thereof.

The complexes of the invention are usefully employed as catalysts for addition polymerization processes to prepare polymers that are useful as molded articles, films for packaging applications, and foams for cushioning applications; and in the modification of synthetic and naturally occurring resins. The complexes may also be used as catalysts for hydrogenations, catalytic cracking processes, and in other industrial applications.

Illustrative atomic arrangements of complexes of the invention as determined from single crystal X-ray diffraction values are shown in Figures 1-3.

Figure 1 shows the single-crystal X-ray crystallographically determined structure of (4-methylphenylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane-titanium dichloride. The angle formed by the centroid of the cyclopentadienyl ring (C2, C3, C5, C7 and C9), the titanium atom (Ti1), and the nitrogen atom (N14) is 105.7°. The centroid of the cyclopentadienyl ring is the average of the respective X, Y, and Z coordinates of the atomic centers forming the ring.

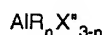
Figure 2 shows the single-crystal X-ray crystallographically determined structure of (phenylamido)-dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane-titanium dichloride. The angle formed by the centroid of the cyclopentadienyl ring (C2, C3, C5, C7, and C9), the titanium atom (Ti1), and the nitrogen atom (N14) was determined to be 106.1°.

Figure 3 shows the single-crystal X-ray crystallographically determined structure of (t-butylamido)-tetramethyl(tetramethyl- η^5 -cyclopentadienyl)disilane-titanium dichloride. The relatively long disilyl linking group that connects the cyclopentadienyl ring to the nitrogen atom of the amide ligand allows the nitrogen atom to be less constrained. The angle formed by the centroid of the cyclopentadienyl ring (C2, C3, C5, C7, and C9), the titanium atom (Ti1), and the nitrogen atom (N17) was determined to be 120.5°. Accordingly, the activity of this catalyst towards olefin polymerization is considerably diminished relative to the analogous monosilane linking group in (t-butyl amido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane-titanium dichloride.

The term "activating cocatalyst" as used herein refers to a secondary component of the catalyst able to cause the metal-containing complex to become effective as an addition polymerization catalyst or alternatively to balance the ionic charge of a catalytically activated species. Examples of the foregoing activating cocatalysts for use herein include aluminum compounds containing an Al-O bond such as the alkylaluminoxanes, especially methylaluminoxane; aluminum alkyls; aluminum halides; aluminum alkylhalides; Lewis acids; ammonium salts; noninterfering oxidizing agents, eg. silver salts, and ferrocenium ions; and mixtures of the foregoing.

Particular techniques for the preparation of aluminoxane type compounds by contacting an aluminum alkyl compound with an inorganic salt containing water of crystallization are disclosed in US-A-4,542,119. In a particularly preferred embodiment an aluminum alkyl compound is contacted with a regeneratable water-containing substance such as hydrated alumina, silica, or other substance. A process for preparing aluminoxane employing such regeneratable substance is disclosed in EP-A-0338,044.

Additional suitable activating cocatalysts include compounds corresponding to the formula:



wherein:

R is each occurrence C_{1-10} alkyl or aralkyl;

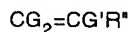
Xⁿ is halogen; and

n is 1, 2 or 3.

Most preferably such cocatalysts are trialkyl aluminum compounds, particularly triethyl aluminum.

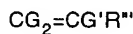
"Addition polymerizable monomers" include, for example, ethylenically unsaturated monomers, acetylenic compounds, conjugated or nonconjugated dienes, and polyenes (eg C_2 - C_{20} polyenes). Preferred monomers include the C_{2-10} α -olefins especially ethylene, propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. Other preferred monomers include styrene, halo- or alkyl substituted styrene, vinyl chloride, acrylonitrile, methyl acrylate, methylmethacrylate, tetrafluoroethylene, methacrylonitrile, vinylidene chloride, vinylbenzocyclobutane, and 1,4-hexadiene.

By the term "hindered aliphatic vinylidene compounds" is meant addition polymerizable vinylidene monomers corresponding to the formula:



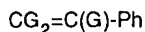
wherein R^{*} is an sterically bulky, aliphatic substituent of up to 20 carbons, G independently each occurrence is hydrogen or methyl, and G' independently each occurrence is hydrogen or methyl or alternatively G' and R^{*} together form a ring system. By the term "sterically bulky" is meant that the monomer bearing this substituent is normally incapable of addition polymerization by standard Ziegler-Natta polymerization catalysts at a rate comparable with ethylene polymerizations. Preferred hindered aliphatic vinylidene compounds are monomers in which one of the carbon atoms bearing ethylenic unsaturation is tertiary or quaternary substituted. Examples of such substituents include cyclic aliphatic groups such as cyclohexane, cyclohexene, cyclooctene, or ring alkyl or aryl substituted derivatives thereof, tert-butyl, and norbornyl. Most preferred hindered aliphatic vinylidene compounds are the various isomeric vinyl-ring substituted derivatives of cyclohexene and substituted cyclohexenes, and 5-ethylidene-2-norbornene. Especially suitable are 1-, 3-, and 4- vinylcyclohexene.

By the term "hindered vinylidene compound" is meant addition polymerizable vinylidene monomers corresponding to the formula:



wherein R'' is R^{*} or an aryl substituent of up to 20 carbons, and G and G' are as previously defined. For example, in addition to hindered aliphatic vinylidene compounds, hindered vinylidene compounds also include the vinylidene aromatic monomers.

By the term "vinylidene aromatic monomers" is meant addition polymerizable compounds corresponding to the formula:



wherein G independently each occurrence is hydrogen or methyl and Ph is phenyl, or a halo- or C₁₋₄ alkylsubstituted phenyl group. Preferred vinylidene aromatic monomers are monomers corresponding to the above formula wherein G each occurrence is hydrogen. A most preferred vinylidene aromatic monomer is styrene.

By the term "α-olefin" is meant ethylene and the C₃₋₁₀ olefins having ethylenic unsaturation in the α-position. Preferred α-olefins are ethylene, propylene, 1-butene, isobutylene, 4-methyl-1-pentene, 1-hexene, and 1-octene, and mixtures thereof.

As previously mentioned, the complexes according to the present invention preferably comprise structures having altered or enhanced catalytic activity at the metal site when the complex is combined with a cocatalyst. In this regard electron donating substituents have been found to improve the catalytic properties of the complexes.

Examples of the above highly preferred metal coordination compounds include compounds wherein the R' on the amido group is methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, or phenyl; R' on the cyclopentadienyl group each occurrence is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, or phenyl; and X is chloro, bromo, iodo, methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, or phenyl. Specific compounds include: (tert-butylamido)dimethyl(tetramethyl-η⁵-cyclopentadienyl)silanetitanium dichloride and (benzylamido)dimethyl(tetramethyl-η⁵-cyclopentadienyl)silanetitanium dichloride.

The complexes can be prepared by contacting the metal reactant and a group I metal derivative or Grignard derivative of the cyclopentadienyl compound in a solvent and separating the salt byproduct. Suitable solvents for use in preparing the metal complexes are aliphatic or aromatic liquids such as cyclohexane, methylcyclohexane, pentane, hexane, heptane, tetrahydrofuran, diethyl ether, C₁₋₄ alkyl ethers of mono- or diethylene glycol, C₁₋₄ alkyl ethers of mono- or dipropylene glycol, benzene, toluene, xylene, and ethylbenzene, or mixtures thereof.

In a preferred embodiment, the metal compound is MX_{n+1}, ie. M is in a lower oxidation state than in the corresponding compound, MX_{n+2} and the oxidation state of M in the desired final complex. A noninterfering oxidizing agent may thereafter be employed to raise the oxidation state of the metal. The oxidation is accomplished merely by contacting the reactants utilizing solvents and reaction conditions used in the preparation of the complex itself. By the term "non-interfering oxidizing agent" is meant a compound having an oxidation potential sufficient to raise the metal oxidation state without interfering with the desired complex formation or subsequent polymerization processes. A particularly suitable noninterfering oxidizing agent is AgCl.

In order to assist in the handling of the metal compounds employed in the present process corresponding to the formula MX_{n+2}, it may be beneficial first to form a solid adduct thereof by the use of a suitable coordinating agent according to well known techniques in the art. For example, whereas titanium tetrachloride is a fuming liquid which is difficult to handle, one may first form an adduct of TiCl₄ with an ether, tertiary amine, tertiary phosphine or other basic nonprotic compound. The resulting solids may be more easily handled. A preferred coordinating adduct is tetrahydrofuran.

The reactions employed in preparing the metal complex may be conducted either heterogeneously or homogeneously. That is, the various reactants or the resulting product need not be substantially soluble in the solvent mixture. Generally the reactants are contacted under an inert atmosphere for a time from several minutes to several days. Agitation may be employed if desired. The temperature of the reaction is generally from -90°C to 150°C, preferably from -20°C to 70°C.

Suitable catalysts for use according to the present invention are prepared by combining the metal coordination compound and activating cocatalyst compound in any order and in any suitable manner. Preferably the ratio of the coordination complex and cocatalyst on a molar basis is from 1:0.1 to 1:10,000. It will, of course, be appreciated that the catalyst system may also be formed in situ if the components thereof are added directly to the polymerization process and a suitable solvent or diluent, including condensed monomer, is used in said polymerization process. Suitable solvents include toluene, ethylbenzene, alkanes and mixtures thereof. In certain cases the catalysts may be isolated from solution and retained under inert atmosphere prior to use. The catalysts' components are sensitive to both moisture and oxygen and should be handled and transferred in an inert atmosphere such as nitrogen, argon or helium or under vacuum.

The polymerization is usually conducted according to known techniques for Ziegler-Natta or Kaminsky-Sinn type polymerizations. That is, the monomer(s) and catalyst are contacted at a temperature from -30°C to 250°C, at reduced, elevated or atmospheric pressures. The polymerization is conducted under an inert atmosphere which may be a blanketing gas such as nitrogen, argon, hydrogen, or ethylene, or under vacuum. Hydrogen may additionally be utilized in the control of molecular weight through chain termination as is previously known in the art. The catalyst may be used as is or supported on a suitable support such as alumina, MgCl₂ or silica to provide a heterogeneous supported catalyst. A solvent may be employed if desired. Suitable solvents include toluene, ethylbenzene, and excess vinylidene aromatic

or olefin monomer. The reaction may also be conducted under solution or slurry conditions, in a suspension utilizing a perfluorinated hydrocarbon or similar liquid, in the gas phase, ie. utilizing a fluidized bed reactor, or in a solid phase powder polymerization. A catalytically effective amount of the present catalyst and cocatalyst are any amounts that successfully result in formation of polymer. Such amounts may be readily determined by the routine experimentation by the skilled artisan. Preferred amounts of catalyst and cocatalyst are sufficient to provide an equivalent ratio of addition polymerizable monomer:catalyst of from 1×10^{10} :1 to 100:1, preferably from 1×10^8 :1 to 500:1, most preferably 1×10^6 :1 to 1000:1. The cocatalyst is generally utilized in an amount to provide an equivalent ratio of cocatalyst:catalyst from 10,000:1 to 0.1:1, preferably from 1,000:1 to 1:1.

It is to be understood that the metal complex may undergo various transformations or form intermediate species prior to and during the course of a polymerization. Thus other precursors could possibly be conceived to achieve the same catalytic species as are herein envisioned without departing from the scope of the present invention.

The resulting polymeric product is recovered by filtering or other suitable technique. Additives and adjuvants may be incorporated in the polymers of the present invention in order to provide desirable characteristics. Suitable additives include pigments, UV stabilizers, antioxidants, blowing agents, lubricants, plasticizers, photosensitizers, and mixtures thereof.

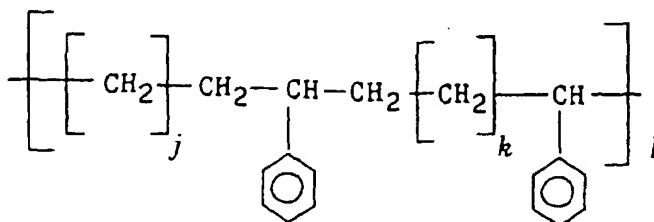
In the preparation of copolymers containing vinylidene aromatic or hindered aliphatic vinyl monomers it is desirable that a comonomer that is an α -olefin that is not particularly sterically hindered also be employed. Without wishing to be bound by any particular theory of operation, it is believed this is because the active site becomes crowded with the incorporation of the hindered vinyl compound making it unlikely that another hindered vinyl compound could enter into the polymerization as the next monomer in the sequence. After the incorporation of one or more olefins other than a hindered vinyl compound the active site once again becomes available for inclusion of a hindered vinyl monomer. On a limited basis however, the vinylidene aromatic monomer or sterically hindered vinyl monomer may insert into the polymer chain in reverse order, ie. so as to result in two methylene groups between the substituted polymer backbone moiety.

Preferably such polymers possess a Mw of greater than 13,000, more preferably greater than 20,000 and most preferably greater than 30,000. Also preferably such polymers possess a melt index (I_2), ASTM D-1238 Procedure A, condition E, of less than 125, more preferably from 0.01 - 100 and most preferably from 0.1 to 10.

Due to the use of the previously mentioned catalyst system comprising a coordination complex of the invention, copolymers may be prepared that incorporate relatively bulky or hindered monomers in substantially random manner at low concentrations, and at higher concentrations according to an ordered insertion logic. The copolymers of α -olefins, especially ethylene and a hindered aliphatic vinylidene compound or vinylidene aromatic monomer can further be described as "pseudo-random". That is, the copolymers lack well defined blocks of either monomer, however the respective monomers are limited to insertion according to certain rules.

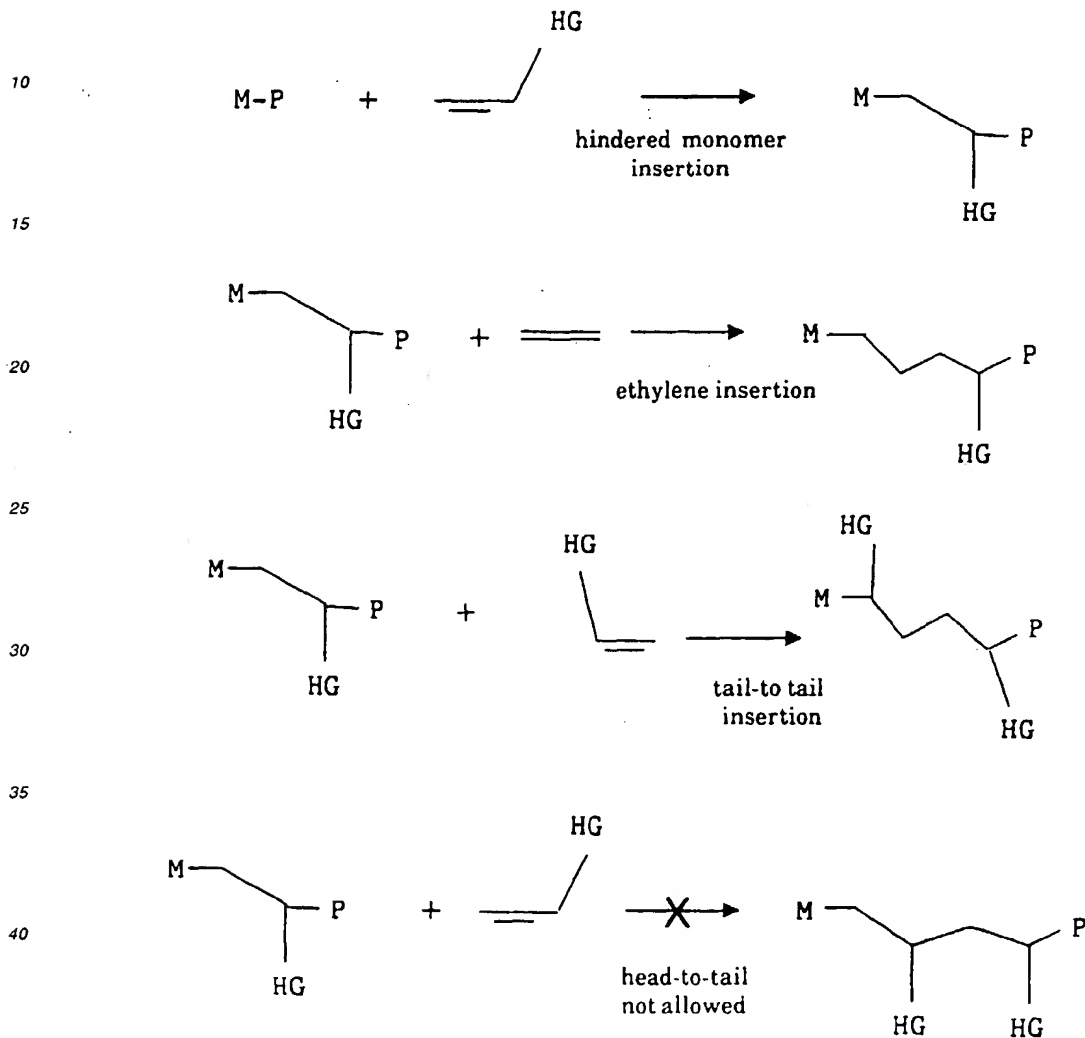
These rules were deduced from certain experimental details resulting from an analysis of the polymers. The polymers were analyzed by ^{13}C NMR spectroscopy at 130°C with a Varian VXR-300 spectrometer at 75.4 MHz. Samples of 200 to 250 mg polymer were dissolved in 15 mL of hot o-dichlorobenzene/1,1,2,2-tetrachloroethane- d_2 (approximately 70/30, v/v) which was approximately 0.05 M in chromium (III) tris(acetylacetonate) and a portion of the resulting solution was added to a 10 mm NMR tube. The following parameters and conditions were used: spectral width, 16,500 Hz; acquisition time 0.090 s; pulse width, 36° ; delay, 1.0 s with the decoupler gated off during the delay; FT size 32K; number of scans, >30,000; line broadening, 3Hz. Spectra, as recorded were referenced to tetrachloroethane- d_2 (873.77 ppm, TMS scale).

Therefor, without wishing to be bound by any particular theory, the results of the foregoing experimental procedures indicate that a particular distinguishing feature of pseudo-random copolymers is the fact that all phenyl or bulky hindering groups substituted on the polymer backbone are separated by 2 or more methylene units. In other words, the polymers comprising a hindered monomer of the present invention can be described by the following general formula (using styrene as the hindered monomer for illustration):



where j , k , and $l \geq 1$

In further explanation of the foregoing experimental and theoretical results, and without wishing to be bound by any particular theory it can be concluded that during the addition polymerization reaction employing the present catalysts, if a hindered monomer is inserted into the growing polymer chain, the next monomer inserted must be ethylene or a hindered monomer which is inserted in an inverted or "tail-to-tail" fashion. This is illustrated below for a hindered vinyl monomer where M is the catalyst metal center, HG is a hindering group, and P is the growing polymer chain:



During the polymerization reaction, ethylene may be inserted at any time. After an inverted or "tail-to-tail" hindered monomer insertion, the next monomer must be ethylene, as the insertion of another hindered monomer at this point would place the hindering substituent closer together than the minimum separation as described above. A consequence of these polymerization rules is the catalysts of this invention do not homopolymerize styrene to any appreciable extent, while a mixture of ethylene and styrene is rapidly polymerized and may give high styrene content (up to 50 mole percent styrene) copolymers.

As a further illustration of the description of the α -olefin/hindered monomer copolymer of the present invention, a computer model of the polymerization reaction was used to calculate the expected ^{13}C NMR spectrum of the polymer product. The computer program utilized a random number generator to select either α -olefin or hindered monomer to be inserted into a growing polymer chain, then calculated the number of each type of ^{13}C NMR signals resulting from that insertion. Polymers were computer generated by repeating this process for 10,000 or more monomer insertions, and the resulting calculated ^{13}C NMR spectrum was compared to actual experimental ^{13}C NMR spectra for pseudo-random ethylene/styrene copolymers of the invention.

Computer simulations of the polymer and resulting ^{13}C NMR spectra of the calculated pseudo-random ethylene/styrene copolymers were performed using the constraint that if styrene monomer were inserted into the growing polymer chain, the next monomer inserted must be ethylene or a styrene which is inserted in an inverted or "tail-to-tail" fashion. Optimum fits between experimental and calculated spectra were obtained if approximately 15 percent of the styrene insertions are in the "tail-to-tail" manner. The observed and calculated ^{13}C NMR spectra for such pseudo-random ethylene/styrene copolymers containing 1.4, 4.8, 9.0, 13, 37, and 47 mole percent styrene are shown in Figures 4-9. In each case, the observed and calculated spectra are in excellent agreement.

Computer simulation of the polymer and resulting ^{13}C NMR spectra of completely random α -olefin/hindered monomer copolymers were then performed using no constraints on hindered monomer insertion. In other words, the hindered monomer was allowed to insert into the growing polymer chain after a previous hindered monomer insertion if the random number generator selected hindered monomer as the next monomer to be inserted. The calculated spectra for these completely random copolymers do not agree with the observed ^{13}C NMR spectra, as shown in Figure 10 for a 37 mole percent styrene containing ethylene/styrene copolymer.

Prior to polymerization according to the present process the monomers and solvents, if any, may be purified by vacuum distillation, and/or contacted with molecular sieves, silica, or alumina to remove impurities. In addition, reactive blanking agents, such as trialkylaluminum compounds, alkali metals and metal alloys, especially Na/K, may be used to remove impurities.

Suitable vinylidene aromatic monomers which may be employed according to the present invention include styrene as well as α -methyl styrene, the C_1 - C_4 alkyl- or phenyl-ring substituted derivatives of styrene, such as ortho-, meta-, and para-methylstyrene, or mixtures thereof, the ring halogenated styrenes, vinylbenzocyclobutanes, and divinylbenzene. A preferred vinylidene aromatic monomer is styrene.

In the polymerization of vinylidene aromatic monomers or hindered aliphatic vinylidene compounds and olefins the monomers are preferably combined in a proportion so as to achieve a vinylidene aromatic monomer (or hindered aliphatic vinylidene compound) content of at least 1.0 mole percent in the resulting polymer more preferably from 1.5 to less than 50 mole percent, highly preferably 5.0 to 48 mole percent, and most preferably from more than 8.0 up to 47 mole percent. Preferred operating conditions for such polymerization reactions are pressures from atmospheric to 1000 atmospheres (0.1 MPa to 100 MPa) and temperatures from 30°C to 200°C . Polymerizations at temperatures above the autopolymerization temperature of the respective monomers may contain small amounts of homopolymer polymerization products resulting from free radical polymerization.

Certain of the polymers prepared according to the present invention, especially copolymers of ethylene and an α -olefin other than ethylene, are characterized by unique rheological properties. In particular, it has been found that the polymers (hereinafter called Elastic Polyethylenes or EIPEs) are less Newtonian than conventionally prepared linear polyethylene resins of similar olefin content. The polymers also have higher elastic modulus particularly at high melt indices compared to such conventional polymers. This property makes the resin especially useful in the formation of films, foams and fabricated articles, for example by blow molding techniques. The above phenomenon is more particularly defined by reference to Figure 11 wherein complex viscosity, η^* measured in poise at 190°C , is plotted as a function of shear rate, ω , measured in radians per second for a typical EIPE copolymer of ethylene and 1-octene according to the invention. The slope of this curve indicates the melt is highly non-Newtonian. The actual values of η^* and ω utilized in the graph are:

η^*	ω	η^*	ω	η^*	ω
1.962×10^5	0.01000	3.230×10^4	0.2512	1.088×10^4	6.310
1.511×10^5	0.01585	2.713×10^4	0.3981	9.336×10^3	10.000
1.115×10^5	0.02512	2.293×10^4	0.6310	7.964×10^3	15.850
8.292×10^4	0.03981	1.966×10^4	1.0000	6.752×10^3	25.120
6.322×10^4	0.06310	1.701×10^4	1.5850	5.677×10^3	39.810
4.920×10^4	0.10000	1.464×10^4	2.5120	4.721×10^3	63.100
3.956×10^4	0.15850	1.265×10^4	3.9810	3.854×10^3	100.000

Also plotted in Figure 11 is the $\tan \delta$ value of the same EIPE polymer. This value is unitless and is calculated by dividing the viscous modulus value by the elastic modulus. The actual values of $\tan \delta$ and ω utilized in the graph are:

$\tan \delta$	ω	$\tan \delta$	ω	$\tan \delta$	ω
0.5526	0.01000	1.243	0.2512	1.718	6.310
0.5231	0.01585	1.381	0.3981	1.677	10.000

(continued)

$\tan \delta$	ω	$\tan \delta$	ω	$\tan \delta$	ω
0.5771	0.02512	1.543	0.6310	1.620	15.850
0.6597	0.03981	1.615	1.0000	1.552	25.120
0.7971	0.06310	1.690	1.5850	1.475	39.810
0.9243	0.10000	1.729	2.5120	1.398	63.100
1.080	0.15850	1.737	3.9810	1.315	100.000

For improved performance in melt blowing applications preferably the $\tan \delta$ value is from 0.1 to 3.0 for shear rates between 0.01-100 radian/sec.

A further property of EIPE polymers is illustrated by reference to Figure 12. The elastic modulus in dynes/cm², G' , at 0.1 radian/sec., and 190°C for several ethylene/ 1-octene EIPE resins is plotted as a function of melt index. The resins utilized include those of Examples 6, 7, 9-11, 13-17, 19-21, 25 and 26.

The values of melt index and elastic modulus utilized in the graph are as follows:

Melt Index	Elastic Modulus	Melt Index	Elastic Modulus	Melt Index	Elastic Modulus
0.10	98760	3.34	4381	18.42	9669
0.15	35220	5.34	5858	31.2	4516
0.18	35920	6.38	10480	31.53	5012
0.22	14270	10.12	5276	31.69	3238
0.45	11140	10.66	6222	41.02	2972
1.72	3003	16.28	2697	-	-
2.46	10620	16.32	6612	-	-

Typical properties of η^* and ω for a conventionally prepared polyethylene resin are provided in Figure 13 for comparison purposes.

It is readily seen that EIPE resins are characterized by high elastic modulus in the melt. In particular, EIPE resins have a melt index (I_2), ASTM D-1238 Procedure A, condition E), less than 200, preferably less than 125, most preferably less than 50 and an elastic modulus greater than 1000 dyne/cm², more preferably greater than 2000 dyne/cm². All of the foregoing rheological measurements are performed by standard techniques such as are disclosed in H. A. Barnes et al., Introduction to Rheology, Elsevier, publishing, Inc., 1989. Densities normally range from 0.85 to 0.97 g/ml, preferably from 0.89-0.97 g/ml. Molecular weight distributions (M_w/M_n) are greater than 2.0, preferably from 3.0-10.0. Typically melting points range from 50°C to 135°C.

Preferred polymers additionally demonstrate properties of homogeneous polymers as defined in US-A-3,645,992, ie. ethylene copolymers having substantially random comonomer distribution within a given molecule and substantially the same ethylene/comonomer ratio between molecules. Polymers produced at elevated polymerization temperatures, especially temperatures greater than 130°C, may exhibit a heterogeneous melt curve. The polymers of the invention are further marked by high clarity. In particular the polymers have better optical properties, especially lower haze than typical ethylene polymers, making them especially well suited for film and injection molding applications.

In addition those polymers comprising an olefin and a vinylidene aromatic monomer, especially ethylene and styrene, have surprisingly been found to possess elastomeric properties. Thus, such polymers are uniquely suited for use in applications for thermoplastic elastomers such as impact modification of thermoplastic and thermosetting polymers including bitumens; adhesives; elastomeric moldings; etc.

The polymers of the invention may be modified by typical grafting, crosslinking, hydrogenation, functionalizing, or other reactions well known to those skilled in the art. With particular regard to the polymers comprising vinylidene aromatic, vinylcyclohexene, or 1,4-hexadiene functionality, the same may be readily sulfonated or chlorinated to provide functionalized derivatives according to established techniques. Additionally, the vinylcyclohexene based polymers are readily crosslinkable by reaction of the unsaturated ring functionality.

The polymers of the present invention, whether or not further modified, may be blended with synthetic or natural polymers to provide blends having desirable properties. In particular polyethylene, ethylene/ α -olefin copolymers, polypropylene, polystyrene, styrene/acrylonitrile copolymers (including rubber modified derivatives thereof), syndiotactic polystyrene, polycarbonate, polyamide, aromatic polyester, polyisocyanate, polyurethane, polyacrylonitrile, silicone, and polyphenyleneoxide polymers may be blended with the polymeric compositions of the present invention. The polymeric modifier is utilized in amounts from 0.1 to 99.0 preferably 0.5 to 50 weight percent.

In a highly preferred embodiment of the invention the polymers containing ethylene and styrene are elastomeric as defined in the definition of an elastomeric substance by ASTM Special Technical Bulletin No. 184 as a substance that can be stretched at room temperature to twice its length and will return to its original length upon release.

In addition to modification of synthetic thermoplastics the present polymers are also usefully employed as modifiers for asphalt or bitumen compositions. Desirably the polymers of styrene/ethylene are utilized in this manner.

The term "bitumen" can generally be defined as mixtures of hydrocarbons of natural or pyrogenous origin or combinations of both, frequently accompanied by their non-metallic derivatives, which may be gaseous, liquid, semi-solid or solid, and which are usually soluble in carbon disulfide. For the purposes of the present invention, bitumen of a liquid, semi-solid or solid nature may be utilized. From a commercial standpoint, bitumen is generally restricted to asphalts and tars and pitches. A listing of various bituminous materials which can be utilized in the present invention include the following:

I. Asphalts

1. Petroleum Asphalts

A. Straight-reduced asphalts

1. Atmospheric or reduced-pressure reduction
2. Solvent precipitated, as with propane

B. Thermal asphalts, as residues from cracking operations on petroleum stocks

C. Air-blown asphalts

1. Straight-blown
2. "Catalytic"-blown

2. Native Asphalts

A. With mineral content below 5 percent

1. Asphaltites such as gilsonite, graphamite, and glance pitch
2. Bermudez and other natural deposits

B. With mineral content over 5 percent

1. Rock asphalts
2. Trinidad and other natural deposits

II. Tars and Derivatives

1. Residua from coke-oven-dried coal tars

- A. Coal tars reduced to float grades, as RT (road tar) grades for paving purposes
- B. Coal-tar pitches, with reduction carried out to softening-point grades

2. Residua from other pyrogenous distillates as from water-gas, wood, peat, bone, shale, rosin, and fatty acid tars.

As can be readily appreciated by those skilled in the art, the weight average molecular weight of the various bitumens can vary over a very wide range, for example such as from 500 to 10,000. Additionally, the softening point of the various types of asphalt will also vary such as from 50°F to 400°F (10°C to 205°C).

Of the many types of asphalts which may be utilized, petroleum, and native are desired, with petroleum being preferred. Of the petroleum asphalts, the thermal asphalts are preferred.

The amount of bitumen utilized in the compositions of the invention preferably ranges from 65 to 99 parts by weight with preferred amounts ranging from 80 to 98 parts by weight.

Having described the invention the following examples are provided as further illustrative and are not to be construed as limiting. Unless stated to the contrary parts and percentages are based on weight.

Example 1 Preparation of (Tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)-silanetitanium dichloride

Preparation 1

(a) (Chloro) (dimethyl) (tetramethylcyclopentadi-2,4-enyl)-silane

To a solution of 21.5 g (167 mmol) dimethyldichlorosilane in 150 mL THF cooled to -40°C was slowly added a solution of 8.00 g (55.6 mmol) sodium 1,2,3,4-tetramethylcyclopentadienide in 80 mL THF. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The solvent was removed, the residue was extracted with pentane and filtered. The pentane was removed under reduced pressure to give the product as a light-yellow oil. The yield was 10.50 g (88.0%). ^1H NMR (C_6D_6) δ 2.89 (s, 1H), 1.91 (s, 6H), 1.71 (s, 6H), 0.14 (s, 6H); ^{13}C NMR (C_6D_6) δ 137.8, 131.5, 56.6, 14.6, 11.4, 0.81.

(b) (Tert-butylamino) (dimethyl) (tetramethylcyclopentadi-2,4-enyl)silane

A solution of 11.07 g (151 mmol) t-butyl amine in 20 mL THF was added during 5 minutes to a solution of 13.00 g (60.5 mmol) (chloro) (dimethyl) (tetramethylcyclopentadienyl)silane in 300 mL THF. A precipitate formed immediately. The slurry was stirred for 3 days, then the solvent was removed, the residue was extracted with pentane and filtered. The pentane was removed under reduced pressure to give the product as a light-yellow oil. The yield was 14.8 g (97.2%). MS: 251 ^1H NMR (C_6D_6) δ 2.76 (s, 1H), 2.01 (s, 6H), 1.84 (s, 6H), 1.09 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (C_6D_6) δ 135.4, 133.2, 57.0, 49.3, 33.8, 15.0, 11.2, 1.3.

(c) Dilithium (tert-butylamido)(dimethyl)-(tetramethylcyclopentadienyl)silane

To a solution of 3.000 g (11.98 mmol) (tert-butylamino)(dimethyl)(tetramethylcyclopentadienyl)silane in 100 mL ether was slowly added 9.21 mL of 2.6 M (23.95 mmol) butyl lithium in mixed C_6 alkane solvent. A white precipitate formed and the reaction mixture was stirred overnight, then filtered. The solid was washed several times with ether then dried under reduced pressure to give the product as a white powder. The yield was 3.134 g (99.8%).

(d) (Tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane titanium dichloride

0.721 g (3.80 mmol) Of TiCl_4 was added to 30 mL frozen (-196°C) THF. The mixture was allowed to warm to -78°C (dry ice bath). To the resulting yellow solution was slowly added a solution of 1.000 g (3.80 mmol) dilithium (tert-butylamido)(dimethyl)tetramethylcyclopentadienyl)silane in 30 mL THF. The solution was allowed to warm to room temperature while stirring overnight. The solvent was removed from the resulting very dark solution. The residue was extracted with pentane and filtered. Cooling in a freezer caused the separation of a very soluble dark reddish-brown material from a light yellow-green crystalline solid. The solid was filtered out and recrystallized from pentane to give the olive-green product. The yield was 0.143 g, 10.2%. ^1H NMR (C_6D_6) δ 2.00 (s, 6H), 1.99 (s, 6H), 1.42 (s, 9H), 0.43 (s, 6H); ^{13}C NMR (C_6D_6) δ 140.6, 137.9, 104.0, 62.1, 32.7, 16.1, 13.0, 5.4.

Preparation 2

In a drybox, 4.0 mL of 2.0 M isopropylmagnesium chloride in diethyl ether was syringed into a 100 mL flask. The ether was removed under reduced pressure to leave a colorless oil. 20 mL of a 4:1 (by volume) toluene:THF mixture was added followed by 0.97 g of (tert-butylamino)dimethyl(tetramethylcyclopentadienyl)silane. The solution was heated to reflux. After 8-10 hours, a white precipitate began to form. After refluxing for a total of 27 hours, the solution was cooled and the volatile materials were removed under reduced pressure. The white solid residue was slurried in pentane and filtered to leave a white powder (1.23 g, 62 percent yield) of $\text{Me}_4\text{C}_5\text{SiMe}_2\text{N-t-BuMg}_2\text{Cl}_2(\text{THF})_2$.

In the drybox, 0.50 g of $\text{TiCl}_3(\text{THF})_3$ was suspended in 10 mL of THF. 0.69 g of solid $\text{Me}_4\text{C}_5\text{SiMe}_2\text{N-t-BuMg}_2\text{Cl}_2(\text{THF})_2$ was added, resulting in a color change from pale blue to deep purple. After 15 minutes, 0.35 g of AgCl was added to the solution. The color immediately began to lighten to a pale green-yellow. After 1 1/2 hours, the THF was removed under reduced pressure to leave a yellow-green solid. Toluene (20 mL) was added, the solution was filtered, and the toluene was removed under pressure to leave a yellow-green microcrystalline solid, 0.51 g (quantitative yield). The product's identity was confirmed as (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitanium dichloride by ^1H NMR, (C_6D_6): δ 1.992 (s), 1.986 (s), 1.414 (s), 0.414 (s).

Preparation 3

TiCl₄, 0.72 g (3.80 mmol) was added to 35 mL of frozen THF (-196°C) in a flask. The mixture was warmed to -78°C. A solution of 1.0 g (3.80 mmol) dilithium (tert-butylamido)dimethyl(tetramethylcyclopentadienyl)-silane in THF was slowly added. The resulting yellow solution was warmed to room temperature and stirred overnight. The solvent was removed to give a dark residue which was extracted with pentane and filtered. The product (C₅Me₄(Me₂SiN-t-Bu)TiCl₂) was obtained as a dark greenish-yellow crystalline material after being recrystallized twice from pentane at -35 to -40°C. Identification was confirmed by ¹³C and ¹H NMR.

Preparation 4

In the drybox, TiCl₃(THF)₃ (2.0 g, 5.40 mmol) was suspended in 40 mL of THF. Dilithium (tert-butylamido)-dimethyl(tetramethylcyclopentadienyl)silane (1.42 g, 5.39 mmol) was then added, resulting in an immediate darkening of the color, eventually to a deep blue. After 1 1/2 hours of stirring, AgCl (0.84 g, 5.86 mmol) was added. The color immediately began to lighten to a red/orange. After 1 1/2 hours of stirring, the THF was removed under reduced pressure. Diethyl ether (50 mL) was added, the solution was filtered, and the volatile materials were removed under reduced pressure. This yielded 1.91 g of the product (tert-butylamido)dimethyl(tetramethyl-η⁵-cyclopentadienyl)-silanetitanium dichloride. ¹H NMR (C₆D₆): δ 1.992 (s), 1.987 (s), 1.415 (s), 0.415 (s).

Polymerization

Polymerization of a styrene/ethylene mixture was accomplished by combining 1.65 mL of a 10 percent solution of MAO in toluene with a solution of 45 mL of toluene and 50 mL styrene in a stainless steel shot tank. 250 μL of a 0.010 M solution of (tert-butylamido)dimethyl(tetramethyl-η⁵-cyclopentadienyl)silanetitanium dichloride was added to 2.5 mL of toluene in a second shot tank. Both shot tanks were sealed, removed from the glove box, and attached to a 600 mL stainless steel pressure vessel. The pressure vessel was evacuated and purged with argon.

The styrene/toluene/MAO solution was added to the pressure vessel and warmed to 89°C under 620 kPa (90 psig) ethylene with stirring. At this time the catalyst solution was added and the pressure was increased to 1275 kPa (185 psig) and regulated between 1240-1275 Kpa (180-185 psig). An exotherm raised the temperature to 95°C. The temperature was lowered to 90°C and was then regulated between 90-92°C for the remainder of the reaction.

After 1.0 h the ethylene feed was discontinued. The reaction was vented to the atmosphere and cooled to 30°C at which time methanol was added. The product was collected, washed with methanol and residual solvents were removed under reduced pressure at 120°C which resulted in 9.02 g of material. ¹³C NMR analysis of this material showed it to be a random copolymer of styrene (15.2 percent on a molar basis) and ethylene, free of peaks attributed to polystyrene.

Example 2 (Olefin Polymerization)

Ethylene was polymerized by combining 5 mL of a 1 M solution of triethyl aluminum in mixed C₆ alkane solvent and 0.5 mL of a 0.01 M solution of (tert-butylamido)-dimethyl(tetramethyl-η⁵-cyclopentadienyl)silanetitanium dichloride in toluene in a stainless steel (SS) shot tank. The titanium catalyst and triethyl aluminum cocatalyst solution was then added under pressure to a 3 L SS pressure vessel containing 2 L of mixed alkane solvent (Isopar™ E, available from Exxon Chemicals, Inc.) under 3100 kPa (450 psig) ethylene at 150°C. The reaction temperature was maintained at 150°C for 10 minutes. The ethylene pressure was held constant, and a mass-flow meter measured the uptake of ethylene to be 15.7 g. The polymer solution was then removed from the pressure vessel and the polyethylene was recovered after drying under reduced pressure at 90°C overnight. Yield was 15.7 g.

Example 3 (Ethylene Homopolymerization)

A SS shot tank was charged with 500 μL (5.0 mmol) of a 0.010 M toluene solution of (tert-butylamido)-dimethyl(tetramethyl-η⁵-cyclopentadienyl)silanetitanium dichloride and 2.5 mL of toluene in an argon filled glove box. In a second SS shot tank, 5.0 mL of a 1.0 M solution of MAO in toluene was added to 92 mL of toluene. Both shot tanks were sealed, removed from the glove box and attached to a 600 mL pressure vessel. The pressure vessel was evacuated and flushed with argon and then flushed with ethylene. The cocatalyst solution was added to the pressure vessel and heated to 89°C under an ethylene pressure of 620 kPa (90 psig). The catalyst solution was added to the reactor at this time. The temperature rose to 109°C within seconds as a result of an exothermic reaction. The ethylene pressure was regulated between 1240-1275 kPa (180-185 psig). After 0.5 hours the reactor temperature had increased to about 110°C and the uptake of ethylene increased. After 1.0 hours ethylene feed was discontinued, the reactor was vented

to the atmosphere, and allowed to cool. The pressure vessel was opened, quenched with methanol, and the polymer was isolated. After removing the volatile components, the yield of polyethylene was 24 g.

Example 4 (Ethylene/Styrene Copolymerization)

In a glove box under argon atmosphere, 8 mL of 15 percent methylaluminoxane (MAO) in toluene (1000 Al:Ti), 150 mL mixed alkane solvent, and 500 mL styrene was added to a stainless steel (SS) shot tank fitted with ball valves on both ends. In another SS shot tank 20 μ mol of anilidodimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitanium dichloride in toluene was added to 2 mL toluene.

The shot tanks were sealed, removed from the glove box and attached to a 600 mL SS pressure vessel. The pressure vessel was evacuated and purged with argon. The content of the first shot tank was added to the pressure vessel, warmed to 90°C and saturated with 1240 kPa (180 psig) ethylene with stirring. At this time the catalyst solution was added from the second shot tank. Ethylene was provided on demand at 1240 kPa (180 psig).

After 60 minutes the ethylene feed was discontinued, the reactor cooled to 30°C, vented to the atmosphere, and the reaction was quenched with acidified methanol. The solution was drained from the reactor into a container which had a small amount of antioxidant. The polymer was dried under vacuum. The polymer yield was 26.6 g, melt index (I_2) = 26.6. ^{13}C NMR analysis indicated the polymer was 47 mole percent styrene (76 weight percent). No isotactic, atactic, or syndiotactic sequences were observed.

Example 5 Ethylene/Styrene Copolymerization

The reaction conditions of Example 4 were substantially repeated to prepare styrene/ethylene copolymers having differing styrene content. The catalyst was (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitanium dichloride except where noted. MAO cocatalyst was employed in an amount to provide an Al:M atomic ratio of 1000:

1. Reaction conditions are contained in Table I.

Table I

Run	mg (complex)	T (°C)	Solvent, amt. (mL) ^b	Ethylene Pressure kPa (psig)	Styrene (mL)	Time (h)	Yield (g)	mol % Styrene	Mw	Mw/ Mn
1	0.92	90	T, 50	1240 (180)	50	1.0	9	15.2	147,000	2.5
2	2.50	90	T, 138	"	138	2.0	29	18.4	65,100	2.7
3	2.20	90	T, 160	"	80	2.0	27	11.7	70,100	2.6
4	2.20	90	T, 204	"	36	2.0	30	8.1	72,300	2.5
5	3.70	90	1,350	1515 (220)	350	1.0	57	10.3	121,000	2.8
6	3.70	90	1,525	"	175	0.75	70	6.8	304,000	2.6
7	3.70	90	1,600	"	100	0.33	46	4.8	180,000	2.6
8	3.70	90	1,440	"	260	0.33	43	9.0	172,000	2.5
9	1.90	90	1,650	"	50	0.5	12	2.5	113,000	3.2
10	1.90	90	1,650	"	50	0.5	40	2.8	164,000	2.6
11	2.20	90	T, 180	1240 (180)	60	2.0	30	13.3	78,600	3.1
12 ^a	2.30	90	T, 180	"	60	2.0	11	37.0	-	-

a. catalyst was (phenylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane titanium dichloride

b. T = toluene, l = mixed alkanes

Examples 6 - 27

In these examples, a 4 liter autoclave was charged with 2000 mL of mixed alkane solvent (Isopar-E) followed by various amounts of 1-octene. The catalyst was (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)-silane titanium dichloride, dissolved in toluene. The cocatalyst was a 10 percent solution of MAO in toluene. Hydrogen, if desired, was added by expansion from a 100 mL vessel at a pressure indicated above the operating pressure of the reactor. The reactor was filled with solvent, 1-octene and MAO, heated to the reaction temperature, then pressurized to 3100 kPa (450 psig) with ethylene until the solution was saturated. The hydrogen (if any) was expanded into the reactor, followed by the addition of the catalyst solution. After 10 minutes, the solution was drained from the reactor into a

EP 0 416 815 B1

container which had a small amount of antioxidant (Irganox 1010-, available from Ciba-Geigy). The polymer was dried under vacuum. Results are contained in Table II.

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Table II

Ex.	Reactor Temp (°C)	Octeno (mL)	ΔH_2 kPa ^a /(psig)	Catalyst mmoles	Al:Ti ^b	Polymer Yield (g)	Mw	Mn	Mw/Mn	Melt Point °C	Density g/mL	Melt Index ^c
6	140	300	0	0.02	500:1	182			-	91	0.9083	1.72
7	160	300	0	0.02	"	61	50,900	12,800	3.98	95 ^d	0.9177	16.28
8	140	300	690 (100)	0.02	"	167	67,500	14,900	3.86	96	0.9176	7.91
9	160	300	"	0.02	"	58	38,500	10,700	3.60	100 ^d	0.9230	31.69
10	140	150	345 (50)	0.02	"	128	66,500	17,400	3.82	105	0.9174	3.34
11	160	150	"	0.02	"	90	53,000	13,400	3.96	106 ^d	0.9317	10.66
12	140	450	"	0.02	"	148	71,700	17,100	4.19	86	0.9010	3.84
13	160	450	"	0.02	"	55	42,500	11,400	3.73	90 ^d	0.9045	31.20
14	150	150	0	0.02	"	75	71,700	16,500	4.35	108	0.9276	2.46
15	150	150	690 (100)	0.02	"	85	44,900	13,400	3.35	108	0.9261	18.42
16	160	450	0	0.02	"	107	62,500	14,800	4.22	92 ^d	0.9090	6.34
17	150	450	690 (100)	0.02	"	85	58,200	12,900	4.51	124	0.9516	6.38
18	150	300	345 (50)	0.02	"	100	51,000	14,000	3.64	95 ^d	0.9130	13.62
19	150	300	"	0.02	"	93	63,700	14,700	3.65	96 ^d	0.9121	10.12
20	150	300	690 (100)	0.02	"	115	43,000	14,200	3.03	96 ^d	0.9118	31.63
21	130	150	345 (50)	0.02	"	166	105,000	23,200	4.53	109	0.9198	0.18
22	130	150	"	0.02	250:1	147	136,000	29,400	4.63	110	0.9197	0.15
23	130	150	"	0.02	100:1	83	146,000	26,300	5.55	105	0.9153	0.16
24	110	150	"	0.01	250:1	98	161,000	42,000	3.83	106	0.9140	0.15
25	120	300	"	0.02	"	123	112,000	28,500	3.93	89	0.9016	0.46
26	110	450	"	0.02	"	145	130,000	37,400	3.48	76	≤0.9000	0.22
27	110	300	"	0.02	"	160	141,000	36,600	3.96	82	≤0.9000	0.16

a. hydrogen partial pressure

b. equivalent ratio assuming 68 MW for MAO

c. 1, ASTM D-1238 Procedure A, condition E.

Examples 28 - 42

The procedure of Examples 6-27 was substantially followed except that a 2000 mL reactor was used. The catalyst was (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane titanium dichloride (2 mL of a 0.005 M solution in toluene, 10 μ moles). The cocatalyst was 15 percent MAO in toluene (2 mL, 500 Al:Ti). Results are contained in Table III.

Table III

Example	Temp, °C	ΔH_f , kPa ^a (psig)	1-Octene mole	g Polymer	Melt Index ^b	Density
28	100	170 (25)	1.59	70.0	<.1	0.8700
29	80	"	1.59	67.7	<.1	0.8672
30	90	"	1.85	98.2		0.8582
31	100	"	2.12	118.3	0.96	0.8575
32	100	345 (50)	1.85	131.9	7.48	0.8552
33	80	170 (25)	2.12	139.3	0.93	0.8528
34	90	0	1.59	104.4	0.25	0.8594
35	90	345 (50)	2.12	133.1		0.8556
36	90	170 (25)	1.85	130.2		0.8550
37	100	0	1.85	110.0	0.66	0.8570
38	90	170 (25)	1.85	141.0		0.8545
39	80	345 (50)	1.85	161.2	5.44	0.8525
40	80	0	1.85	118.1	0.48	0.8536
41	90	0	2.12	150.8	3.12	0.8516
42	90	345 (50)	1.59	136.7	3.43	0.8578

a. hydrogen partial pressure

b. I₂, ASTM-D-1238 Procedure A, condition E.

Examples 43 - 52 Olefin polymerization

Ethylene and/or ethylene/1-octene were respectively polymerized as a homopolymer or copolymer by adding a solution of the appropriate catalyst in combination with MAO or triethyl aluminum cocatalyst to a 3L SS pressure vessel containing mixed C₆ alkane solvent/1-octene (with varying ratios) under 3100 kPa (450 psig) of ethylene at 150°C (or 175°C where indicated) for 10 minutes. The ethylene pressure was held constant and a mass flow meter measured the uptake of ethylene. The consequent polymer was then removed from the pressure vessel and dried under reduced pressure at 90°C overnight. Results are contained in Table IV.

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Table IV

Example	Catalyst ^{a,b}	Solvent/ Octene ^c	Wt. of polymer (g)	Melt Index $\frac{I_2}{I_1}$	MW	Mn	Mw/Mn
43	Ti	1/1	61.1	79.0	45,600	9100	5.01
44	Ti	2/0.3	48.7	1.7	88,300	10100	8.74
45	Ti	1/1	41.5	137.6	36,300	9950	3.68
46	Ti	2/0	15.6	4.4	--	--	--
47	Ti	1/1	47.5	25.8	54,000	10800	5.00
48	Ti	2/0.3	74.5	56.3	44,400	12100	3.67
49	Ti	2/0.3	75.0	56.9	44,700	9800	4.56
50	Ti	2/0	15.6	--	--	--	--
51 ^d	Ti	2/0.15	19.9	--	--	--	--
52	Ti	2/0.15	34.5	1.0	--	--	--

- a) Ti = (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane-titanium dichloride
b) Metal/Al ratio = 1/1000 assuming 58 MW for MAO
c) liters of each
d) Used triethylaluminum as cocatalyst; metal/Al was 1:1000

Example 53 Preparation of Supported (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitanium dichloride

0.100 g of dehydroxylated silica (-OH concentration \approx 1 mmol/g SiO_2) was slurried in 20 mL of mixed C_6 alkane solvent under a nitrogen atmosphere in a dri-box, with stirring in a 50 mL Erlenmeyer flask. From this slurry 1.0 mL was removed by syringe and combined with 1.10 mL of a 0.011 M toluene solution of (tert-butylamido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)dimethylsilane-titanium dichloride in a 5 mL rounded-bottomed flask and stirred for 12 h. After this period 6.7 mL of a 10 percent (w/w) solution of methyl aluminoxane (MAO) in toluene was added to the silica containing solution.

Polymerization

The polymerization was conducted by adding under pressure the above titanium/silica/MAO slurry in a 3 L SS pressure vessel containing 2 L of mixed alkane solvent under 3100 kPa (450 psig) of ethylene at 150°C for 10 minutes. The ethylene pressure was held constant and a mass flow meter measured the uptake of ethylene to be 26.7 g. The polymer solution was then removed from the pressure vessel and the polyethylene was recovered after drying under reduced pressure at 90°C overnight. Yield was 30.0 g.

54 Preparation of (2-Methoxyphenylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitanium dichloride

(a) ((Tetramethylcyclopentadienyl)dimethylsilyl)-(2-methoxyphenyl)amine

To 1.3 g (5.9 mmol) ((tetramethylcyclopentadienyl)dimethylsilyl)chloride in 50 mL tetrahydrofuran (THF) was added 0.86 g (5.9 mmol) sodium 2-methoxyanilide. The mixture was stirred overnight. The solvent was removed under reduced pressure and the residue extracted with pentane. The pentane extracts were filtered, combined, and concentrated to give a pale yellow liquid. Yield 1.4 g (79%). ^1H NMR (benzene- d_6) δ 6.91 (m, 2.2), 6.74 (m, 1.1), 6.57 (d, 1.1, J = 9), 4.25 (s, 1), 3.32 (s, 3.7), 1.93 (s, 6.7), 1.80 (s, 6.8), 0.13 (s, 6.3).

(b) Dilithium ((tetramethylcyclopentadienyl)-dimethylsilyl)-(2-methoxyphenyl)amide.

To 1.4 g (4.6 mmol) ((tetramethylcyclopentadienyl)-dimethylsilyl) (2-methoxyphenyl)amine in diethyl ether was added dropwise 3.9 mL of 2.5 M butyl lithium (9.8 mmol) in hexane solvent. A white precipitate formed. Pentane was added to the mixture. The slurry was filtered and the solids washed with pentane.

(c) (2-Methoxyphenylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitanium dichloride

To 1.6 g of dilithium ((tetramethylcyclopentadienyl)-dimethylsilyl)(2-methoxyphenyl)amide slurried in toluene was added 0.85 g TiCl_4 . The mixture was stirred for three days, filtered, and the solvent was removed under reduced pressure. The residue was slurried in pentane and filtered to give a dark powder. Yield 0.77 g (41%). ^1H NMR (benzene- d_6) δ 4.10 (s, 3), 2.20 (s, 6.4), 1.99 (s, 6.6), 0.40 (s, 6.3).

Example 55 Preparation of (4-Fluorophenylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitanium dichloride (not example of the invention)

(a) ((Tetramethylcyclopentadienyl)dimethylsilyl)-(4-fluorophenyl)amine

Equimolar quantities of ((tetramethylcyclopentadienyl)dimethylsilyl)chloride and lithium 4-fluoroanilide were combined in THF and the mixture stirred overnight. The solvent was removed under reduced pressure. ^1H NMR (benzene- d_6) δ 6.79 (m, 2.5), 6.33 (m, 2.4), 2.95 (s, 1), 2.90 (s, 1), 1.87 (s, 6.9), 1.79 (s, 6.9), 0.02 (s, 5.8).

(b) Dilithium ((tetramethylcyclopentadienyl)-dimethylsilyl)-(4-fluorophenyl)amide

((Tetramethylcyclopentadienyl)dimethylsilyl)-(4-fluorophenyl)amine in diethyl ether solvent and butyl lithium 2.5 M in hexane solvent were combined in equivalent amounts. A white precipitate formed. Pentane was added to the slurry. The precipitate was filtered, washed with pentane and dried. ^1H NMR (THF- d_8) δ 7.28 (m, 2.0), 6.77 (m, 2), 3.27 (s, 2.7), 2.05 (s, 5.2), 2.01 (s, 5.2), 0.44 (s, 4.6).

(c) (4-Fluorophenylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane titanium dichloride

To 0.59 g (1.6 mmol) $\text{TiCl}_3 \cdot 3\text{THF}$ in 50 mL THF was added 0.50 g (1.7 mmol) dilithium ((tetramethylcyclopentadienyl)dimethylsilyl)(4-fluorophenyl)amide. After 0.5 h, 0.25 g (1.8 mmol) AgCl was added. After 2 h the solvent was removed under reduced pressure. The residue was extracted with diethyl ether. The ether extracts were filtered, combined, and concentrated under reduced pressure to give a red glassy solid. Dissolution into toluene and re-concentration produced a waxy solid. This solid was extracted into pentane. The pentane extracts were filtered, combined, and concentrated to produce a waxy solid. This was slurried with a small amount of pentane (2 mL) and filtered to give a red powder. The yield was 0.18 g (28%). ^1H NMR (benzene- d_6) δ 7.10 (t), 6.80 (t), 2.00 (s), 1.97 (s), 0.35 (s).

Polymerization

The polymerization procedure of Examples 6-27 was substantially followed using 1000 mL of mixed alkane solvent, 200 mL of 1-octene and 5 mL of 15 percent MAO in toluene (1280 Al:Ti) and a reaction temperature of 130°C. Hydrogen was supplied from a 75 mL tank pressurized to 3450 kPa (500 psig) to give a delta pressure of 345 kPa (50 psi). 10 Micromoles of the above complex was added to begin the polymerization. Ethylene was provided on demand at 3100 kPa (450 psig). The polymer yield was 12.8 g, $M_w = 103,000$, $M_w/M_n = 4.77$, density = 0.9387, melt index = 6.37.

Example 56 Preparation of ((2,6-Di(1-methylethyl)phenyl)amido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitanium dichloride

Dilithium ((tetramethylcyclopentadienyl)dimethylsilyl)(2,6-di(1-methylethyl)phenyl)amide was prepared in a manner analogous to Example 55.

To 1.5 g (4 mmol) $\text{TiCl}_3 \cdot 3\text{THF}$ in 25 mL THF was added 1.5 g (4 mmol) dilithium ((tetramethylcyclopentadienyl)dimethylsilyl)(2,6-di(1-methylethyl)phenyl)amide. After 0.5 h 0.63 g (4 mmol) AgCl was added. After 1.5 h the solvent was removed under reduced pressure. The residue was extracted with pentane (3 x 8 mL). The pentane insoluble residue was extracted with diethyl ether. The ether extract was filtered and evaporated to dryness to give a yellow crystalline solid. ^1H NMR (benzene- d_6) δ 3.04 (heptet, 2, J = 6.7), 2.18 (s, 5.8), 1.98 (s, 5.8), 1.49 (d, 5.8, J = 6.5), 1.12 (d, 6.2, J = 6.8), 0.48 (s, 5.2).

Polymerization

The polymerization procedure of Example was followed using 10 micromoles of the above complex. The polymer yield was 14.7 g.

Example 57 Preparation of (4-Methoxyphenylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitanium dichloride

To 0.73 g $\text{TiCl}_4 \cdot 2\text{THF}$ in 30 mL toluene was added 0.7 g of dilithium ((tetramethylcyclopentadienyl)dimethylsilyl)-(4-methoxyphenyl)amide (prepared in a method analogous to Example 56). The mixture was stirred for two days, filtered, and concentrated under reduced pressure. The residue was slurried in pentane and filtered to give a brick red powder. Yield 0.61 g (67%). ^1H NMR (benzene- d_6) δ 7.28 (d, 2, J = 8.8), 6.78 (d, 2, J = 8.9), 3.27 (s, 2.8), 2.05 (s, 5.6), 2.01 (s, 5.6), 0.44 (s, 4.8).

Polymerization

The polymerization procedure of Example 55 was followed using 10 micromoles of the above complex. The polymer yield was 7.2 g, $M_w = 79,800$, $M_w/M_n = 21.5$, melt index = 2.90.

Example 58 Preparation of 1-(Tert-butylamido-2-tetramethyl- η^5 -cyclopentadienyl)-1,1,2,2-tetramethyldisilanetitanium dichloride

(a) 1-Chloro-2(tetramethylcyclopentadienyl)-1,1,2,2-tetramethyldisilane

To a solution of 4.802 g (25.7 mmol) 1,2-dichloro-1,1,2,2-tetramethyldisilane in 50 mL dimethylether was slowly added a solution of 2.285 g (12.8 mmol) sodium 1,2,3,4-tetramethylcyclopentadienide in 30 mL dimethylether. The reaction mixture was stirred several hours, then the solvent was removed, the residue was extracted with pentane and filtered. The pentane was removed under reduced pressure to give the product as a light-yellow oil. Mass spec: m/e

272 (8%). ^1H NMR (C_6D_6) δ 2.70 (s, 1H), 1.83 (s, 6H), 1.69 (s, 6H), 0.28 (s, 6H), 0.23 (s, 6H); ^{13}C NMR (C_6D_6) δ 135.8, 134.0, 54.4, 14.6, 11.4, 3.2, -2.4.

(b) 1-(tert-butylamino)-2-(tetramethylcyclopentadienyl)-1,1,2,2-tetramethyldisilane

To a solution of 3.000 g (11.0 mmol) 1-chloro-2-(tetramethylcyclopentadienyl)-1,1,2,2-tetramethyldisilane in 50 mL ether was added 2.422 g (33.1 mmol) tert-butylamine. Precipitate formed rapidly. The slurry was stirred for several days at room temperature, then was gently heated to drive the reaction to completion. The solvent was removed, the residue was extracted with pentane, the amine hydrochloride was filtered and the pentane was removed under reduced pressure to give the product as a yellow oil. The yield was 3.150 (92.5%). Mass spec: m/e 309. ^1H NMR (C_6D_6) δ 2.75 (s, 1H), 1.95 (s, 6H), 1.82 (s, 6H), 1.08 (s, 9H), 0.51 (s, 1H), 0.24 (s, 6H), 0.16 (s, 6H); ^{13}C NMR (C_6D_6) δ 135.2, 134.4, 55.2, 50.3, 34.1, 14.9, 11.6, 3.3, -1.4.

(c) Dilithium 1-(tert-butylamido)-2-(tetramethylcyclopentadienyl)-1,1,2,2-tetramethyldisilane

To a solution of 3.00 g (9.72 mmol) 1-(tert-butylamino)-2-(tetramethylcyclopentadienyl)-1,1,2,2-tetramethyldisilane in 100 mL ether was slowly added 7.70 mL of 2.60 M (20.2 mmol) butyl lithium in mixed C_6 alkane solvent. The resulting slurry was stirred several hours, then filtered and washed with ether, then dried under reduced pressure to give the product as a white powder. The yield was 2.918 g (93.4%). ^1H NMR (THF d_8) δ 2.05 (s, 6H), 1.91 (s, 6H), 0.87 (s, 9H), 0.25 (s, 6H), -0.03 (s, 6H); ^{13}C NMR (THF d_8) δ 117.3, 113.6, 53.5, 38.4, 34.1, 14.2, 11.3, 8.4, 2.2.

(d) 1-(tert-butylamido)-2-(tetramethyl- η^5 -cyclopentadienyl)-1,1,2,2-tetramethyldisilane titanium dichloride

A slurry of 0.7500 g (2.333 mmol) dilithium 1-(tert-butylamido)-2-(tetramethylcyclopentadienyl)-1,1,2,2-tetramethyldisilane and 0.7790 g (2.333 mmol) $\text{TiCl}_4(\text{THF})_2$ in 50 mL toluene was stirred for several days. The red-orange reaction mixture was filtered and the solvent was removed to give a sticky red solid. This was extracted with pentane and filtered. After concentration and cooling at -35°C in a freezer, the shiny microcrystalline red product was collected on a frit and washed with cold pentane to remove a dark red oily material. Yield: 0.3643 g, 36.6%. ^1H NMR (C_6D_6) δ 2.20 (s, 6H), 1.94 (s, 6H), 1.48 (s, 9H), 0.44 (s, 6H), 0.43 (s, 6H). ^{13}C NMR (C_6D_6) δ 137.7, 135.5, 112.7, 65.9, 35.4, 16.6, 12.5, 2.8, -2.1.

Polymerization

The polymerization procedure of Example 55 was followed using 10 micromoles of the above complex. The polymer yield was 12.1 g, $M_w = 62,400$, $M_w/M_n = 8.45$, melt index = 6.14, density = 0.9441.

Example 59 Preparation of Preparation of (tert-butylamido)dimethyl(η^5 -cyclopentadienyl)silane/titanium dichloride

(a) (Chloro) (cyclopentadienyl) (dimethyl)silane

A solution of 149 g (1.16 mol) Me_2SiCl_2 in 750 mL diethyl ether was cooled to -78°C . Solid sodium cyclopentadienide (30 g, 0.341 mol) was added via a powder addition funnel over a period of 1.5 hours. The reaction mixture was allowed to warm to room temperature and was stirred for 16 hours. The ether and some Me_2SiCl_2 were distilled out, then exhaustive vacuum distillation removed the remaining ether, Me_2SiCl_2 and the product from the NaCl formed in the reaction. The product after fractionation was obtained in good yield as a light-yellow oil. Mass spec: m/e 158 (16%).

(b) (Tert-butylamino) (cyclopentadienyl) (dimethyl)silane

To a solution of 3.69 g (50.4 mmol) tert-butyl amine in 45 mL THF was added 2.00 g (12.6 mmol) (chloro) (cyclopentadienyl) (dimethyl)silane. Precipitate formed quickly. The slurry was stirred for several days, then the amine hydrochloride was filtered off and the solvent was removed under reduced pressure to give the product as a very pale yellowish oil. The yield was 2.069 g (84.2%). Mass spec: m/e 195 (6%). ^1H and ^{13}C NMR show the presence of several cyclopentadiene isomers.

(c) Dilithium (tert-butylamido) (cyclopentadienyl)-(dimethyl)silane

To a solution of 1.500 g (7.69 mmol) (tert-butylamido) (cyclopentadienyl) (dimethyl)silane in 60 mL ether was slowly added 6.21 mL of a 1.72 M (10.68 mmol) ether solution of methyllithium, then 1.81 mL of 2.6 M (4.706 mmol) butyllithium

in mixed alkane solvent (15.39 mmol total alkyllithiums). The resulting slurry was stirred overnight, then filtered and washed with pentane, then dried under reduced pressure to give the product as a white powder. The yield was 1.359 g (85.2%). ^1H NMR (THF d_8) δ 5.96 (t, 2H), 5.87 (t, 2H), 1.10 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (THF d_8) δ 114, 105.2, 103.5, 52, 38.3, 7.3.

(d) (Tert-butylamido)dimethyl(η^5 -cyclopentadienyl)silane titanium dichloride

0.7000 g (3.38 mmol) Dilithium (tertbutylamido) (cyclopentadienyl) (dimethyl)silane and 1.128 g (3.38 mmol) $\text{TiCl}_4 \cdot (\text{THF})_2$ were combined in a flask with 75 mL toluene. The resulting yellow slurry turned muddy red-brown within a few hours. The reaction mixture was stirred for several days then the red solution was filtered and the solvents removed under reduced pressure. The crystalline material formed was slurried with pentane and filtered to remove the soluble red impurity from the brown product. The yield was 0.5369 g (50.9%). ^1H NMR (C_6D_6) δ 6.60 (t, 2H), 6.07 (t, 2H), 1.38 (s, 9H), 0.18 (s, 6H). ^{13}C NMR (C_6D_6) δ 126.3, 125.6, 110.0, 63.7, 32.2, -0.2.

Polymerization

The polymerization procedure of Example was followed using 10 micromoles of the above complex. The polymer yield was 28.1 g, $M_w = 108,000$, $M_w/M_n = 3.22$, density = 0.9073, melt index = 2.92.

Example 60 Preparation of (Anilido) (dimethyl) (tetramethyl- η^5 -cyclopentadienyl)silane titanium dichloride

(a) (Anilido)(dimethyl)(tetramethylcyclopentadienyl)-silane

To a solution of 1.500 g (6.98 mmol) (chloro)(dimethyl)(tetramethylcyclopentadienyl)silane in 50 mL THF was slowly added 0.6911 g (6.98 mmol) lithium anilide. Monitoring by GC indicated the reaction was incomplete. Additional lithium anilide (0.08 g, 7.78 mmol total) was added. The reaction mixture was stirred overnight. The solvent was removed, the residue was extracted with pentane and filtered. The pentane was removed under reduced pressure to give the product as a pale yellow oil. The yield was 1.875 g (99.2%). Mass spec. m/e 271 (13%). ^1H NMR (C_6D_6) δ 7.14 (m, 2H), 6.76 (t, 1H), 6.60 (d, 2H), 3.08 (s, 1H), 3.04 (s, 1H), 1.89 (s, 6H), 1.79 (s, 6H), 0.07 (s, 6H). ^{13}C NMR (C_6D_6) δ 147.5, 136.3, 132.6, 129.6, 118.2, 116.9, 55.0, 14.3, 11.3, -2.2.

(b) Dilithium (anilido)(dimethyl)(tetramethylcyclopentadienyl)silane

To a solution of 1.875 g (6.91 mmol) (anilido)(dimethyl)(tetramethylcyclopentadienyl)silane in 50 mL ether was slowly added 5.31 mL of 2.60 M (13.8 mmol) butyllithium in hexane solvent. A small amount of precipitate formed, but then dissolved. The reaction mixture was stirred overnight. The product appeared to have collected as a thick viscous oil in the ether solution. The solvent was removed under reduced pressure. The resulting white solid was slurried in pentane, collected on a frit, washed with pentane and dried under reduced pressure to give the product as a white powder. The yield was 1.943 g (99.3%).

(c) (Anilido) (dimethyl) (tetramethyl- η^5 -cyclopentadienyl)silane titanium dichloride

A slurry of 0.8025 g (2.333 mmol) dilithium (anilido) (dimethyl) (tetramethylcyclopentadienyl)silane and 0.9871 g (2.333 mmol) $\text{TiCl}_4 \cdot (\text{THF})_2$ in 70 mL toluene was stirred for several days. The red-brown reaction mixture was filtered and the solvent was removed. The solid was triturated in pentane and the product was collected on a frit and washed with cold pentane to remove a dark red oily material to give the product as a yellow-beige powder. Yield: 0.6400 g, 55.8%. ^1H NMR (C_6D_6) δ 7.32 (d, 2H), 7.18 (m, 2H), 6.85 (t, 1H), 2.02 (s, 6H), 1.99 (s, 6H), 0.42 (s, 6H). ^{13}C NMR (C_6D_6) δ 152.4, 141.9, 137.8, 129.3, 124.4, 119.6, 105.3, 16.1, 13.0, 2.7.

Polymerization 1

The polymerization procedure of Example 55 was followed using 10 micromoles of the above complex. The polymer yield was 12.8 g, $M_w = 103,000$, $M_w/M_n = 4.77$, density = 0.9387, melt index = 6.37.

Polymerization 2 Ethylene/Styrene Copolymerization

The above polymerization procedure was substantially followed except that 900 mL of mixed alkane solvent, 184 mL of styrene, 345 kPa (50 psi) delta hydrogen, and 20 micromoles of $[(\text{C}_5\text{Me}_4)\text{SiMe}_2(\text{tert-butyl})]\text{TiCl}_2$ were used. The

temperature of the reactor was 120°C. After 10 minutes, the contents were removed from the reactor, and 62.3 g of polymer was recovered. The melt index was 3.68.

Example 61 Preparation of (p-Toluidido) (dimethyl) (tetramethyl- η^5 -cyclopentadienyl)-silanetitanium dichloride

(a) (p-Toluidido) (dimethyl) (tetramethylcyclopentadienyl)-silane

To a solution of 2.000 g (9.302 mmol) (chloro)-(dimethyl) (2,3,4,5-tetramethylcyclopentadienyl)silane in 70 mL THF was slowly added 1.259 g (9.302 mmol) lithium p-toluidide (0.3 ether adduct by ^1H NMR). The reaction mixture was stirred overnight. Monitoring by GC indicated the reaction was incomplete. Additional lithium p-toluidide was added in small lots (0.725 g, 14.7 mmol total). The solvent was removed, the residue was extracted with pentane and filtered. The pentane was removed under reduced pressure to give the product as a yellow oil. The yield was 2.456 g (92.5%). Mass spec. m/e 285 (22%). ^1H NMR (C_6D_6) δ 6.96 (d, 2H), 6.57 (d, 2H), 3.07 (s, 1H), 3.01 (s, 1H), 2.17 (s, 3H), 1.91 (s, 6H), 1.80 (s, 6H), 0.08 (s, 6H). ^{13}C NMR (C_6D_6) δ 145.0, 136.2, 132.7, 130.2, 126.9, 116.9, 55.2, 20.5, 14.3, 11.3, -2.2.

(b) Dilithium (p-toluidino) (dimethyl) (tetramethyl-cyclopentadienyl)silane

To a solution of 2.233 g (7.82 mmol) (p-toluidino) (dimethyl) (tetramethylcyclopentadienyl)silane in 65 mL ether was slowly added 6.17 mL of 2.60 M (16.0 mmol) butyllithium in mixed C_6 alkane solvent. The precipitate-free reaction mixture was stirred overnight. The solvent was removed under reduced pressure. The resulting white solid was slurried in pentane, collected on a frit, washed with pentane and dried under reduced pressure to give the product as a white powder. The yield was 2.34 g (100%). ^1H NMR (THF d-8) δ 6.42 (d, 2H), 6.18 (d, 2H), 2.09 (s, 6H), 2.01 (s, 3H), 1.94 (s, 6H), 0.36 (s, 6H). ^{13}C NMR (THF d-8) δ 160.8, 129.1, 121.3, 115.9, 115.2, 112.2, 106.2, 20.8, 14.7, 11.7, 5.2.

(c) (p-Toluidino) (dimethyl) (tetramethyl- η^5 -cyclopentadienyldienyl)silanetitanium dichloride

A slurry of 1.000 g (3.363 mmol) dilithium (p-toluidino) (dimethyl) (tetramethyl- η^5 -cyclopentadienyl)silane and 1.123 g (3.363 mmol) $\text{TiCl}_4(\text{THF})_2$ in 70 mL toluene. The reaction mixture was stirred several days, then filtered and the solvent was removed. The resulting solid was slurried in pentane and the product was collected on a frit and dried under reduced pressure. The yield of olive-brown powder was 0.7172 g, 53.0%. ^1H NMR (C_6D_6) δ 7.26 (d, 2H), 7.01 (d, 2H), 2.08 (s, 3H), 2.04 (s, 6H), 2.00 (s, 6H), 0.45 (s, 6H). ^{13}C NMR (C_6D_6) δ 150.3, 141.7, 137.5, 133.9, 130.0, 129.7, 119.6, 21.0, 20.6, 16.4, 16.0, 13.3, 12.8, 2.8, 2.6.

Example 62 Preparation of (Benzylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl) silanetitanium dichloride

(a) (Benzylamino) dimethyl (tetramethylcyclopenta-dienyl)silane

To a solution of 1.000 g (4.651 mmol) (chloro) (dimethyl) (tetramethylcyclopentadienyl)silane in 70 mL ether was slowly added 0.526 g (4.651 mmol) lithium benzylamide. The reaction mixture was stirred overnight, then the solvent was removed, the residue was extracted with pentane and filtered. The pentane was removed under reduced pressure to give the product as a pale yellow oil. The yield was 1.234 g (93.3%). Mass spec. m/e 285 (18%). ^1H NMR (C_6D_6) δ 7.0-7.24 (m, 5H), 3.71 (d, 2H), 2.73 (br s, 1H), 1.88 (s, 6H), 1.76 (s, 6H), 0.43 (br t, 1H), -0.07 (s, 6H). ^{13}C NMR (C_6D_6) δ 144.5, 135.7, 132.0, 128.5, 127.3, 126.7, 56.7, 46.4, 14.6, 11.4, -2.3.

(b) Dilithium (benzylamido)dimethyl(tetramethyl--cyclopentadienyl)silane

To a solution of 1.091 g (3.836 mmol) (benzylamino) (dimethyl) (tetramethylcyclopentadienyl)silane in 70 mL ether was slowly added 3.1 mL of 2.60 M (8.06 mmol) butyl lithium in mixed C_6 alkane solvent. A pale pink color forms along with precipitate. The reaction mixture was stirred overnight. The solvent was removed under reduced pressure. The resulting solid was slurried in pentane, collected on a frit, washed with pentane and dried under reduced pressure to give the product as a very pale pink powder. The yield was 1.105 g (96.9%). ^1H NMR (THF d-8) δ 7.15 (m, 4H), 7.00 (t, 1H), 4.02 (s, 2H), 2.04 (s, 6H), 1.79 (s, 6H), -0.15 (s, 6H). ^{13}C NMR (THF d-8) δ 152.1, 128.1, 127.9, 125.0, 115.8, 111.9, 108.3, 54.0, 15.0, 11.2, 4.6.

(c) (Benzylamido) dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitanium dichloride

A slurry of 0.5052 g (1.699 mmol) dilithium (benzylamido) (dimethyl) (tetramethyl- η^5 -cyclopentadienyl)silane and

0.5673 g (1.699 mmol) $\text{TiCl}_4(\text{THF})_2$ in 40 mL toluene was stirred for several days. The dark green-brown reaction mixture was filtered and the solvent was removed. The dark oily residue was slurried in pentane and the product was collected on a frit and washed with cold pentane to remove a dark oily material to give the product as a greenish yellow powder. Yield: 0.2742 g (40.1%). ^1H NMR (C_6D_6) δ 7.19 (m, 2H), 7.02 (m, 3H), 5.37 (s, 2H), 1.99 (s, 6H), 1.98 (s, 6H), 0.03 (s, 6H). ^{13}C NMR (C_6D_6) δ 141.4, 140.9, 135.8, 129.0, 128.8, 126.9, 126.6, 126.3, 111.6, 103.6, 59.3, 15.6, 12.4, 1.7.

Polymerization

The polymerization procedure of Example 55 was followed using 10 micromoles of the above complex. The polymer yield was 14.4 g, Mw/Mn = 5.0, melt index = 251, density = 0.9690.

Example 63 Preparation of (Methylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitanium dichloride

(a) (Methylamino) dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane

To a solution of 1.900 g (8.845 mmol) (chloro)-(dimethyl) (tetramethylcyclopentadienyl)silane in 75 mL THF was quickly added 0.3272 g (8.846 mmol) lithium methylamide. The clear solution was stirred overnight, then additional lithium methylamide (0.008 g, 9.062 mmol total) was added as gas chromatography (GC) indicated the reaction was incomplete and the solution was stirred overnight again. The solvent was removed, the residue was extracted with pentane and filtered, and the pentane was removed under reduced pressure to give the product as a very pale yellow oil. The yield was 1.698 g (91.7%). Mass spec. m/e 209 (13 percent). ^1H NMR (C_6D_6): δ 2.82 (s, 1H), 2.33 (d, J = 6.6 Hz, 3H), 1.95 (s, 6H), 1.83 (s, 6H), -0.04 (s, 6H). ^{13}C NMR (C_6D_6): δ 135.4, 132.7, 56.1, 27.8, 14.0, 11.0, -3.5.

(b) Dilithium (methylamido)dimethyl(tetramethylcyclopentadienyl)silane

To a solution of 1.563 g (7.463 mmol) (methylamino) (dimethyl) (tetramethylcyclopentadienyl) silane in 65 mL ether/pentane (1:1) was slowly added 6.03 mL of 2.60 M (15.7 mmol) butyllithium in mixed C_6 alkane solvent. The solution turned to a thick syrup which broke down to a slurry. The reaction mixture was stirred overnight, then filtered. The solid was washed several times with ether, then with pentane, then dried under reduced pressure to give the product as a white powder. The yield was 1.883 g of a 0.25 ether adduct as determined by ^1H NMR spectroscopy. ^1H NMR (THF d-8) δ 3.41 (q, J = 7.0 Hz, 1H), 2.45 (s, 3H), 2.01 (s, 6H), 1.93 (s, 6H), 1.11 (t, J = 7.01 Hz, .5H), 0.01-0.14 (br, 6H).

(c) (Methylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyldienyl)silanetitanium dichloride

To a solution of 0.6708 g (2.597 mmol) dilithium (methylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane in 80 mL THF was added all at once 0.9623 g (2.597 mmol) $\text{TiCl}_3(\text{THF})_3$. The solution immediately turned intense brown-orange. The reaction mixture was stirred four days, then 1.861 g (12.98 mmol) AgCl was added. The slurry was stirred several days after which the reaction mixture was filtered and the solvents were removed under reduced pressure. The residue was extracted with toluene, the dark orange-brown solution was filtered and the solvent was removed. After extraction with pentane and filtration, the filtrate was concentrated to a light brown slurry in a dark red solution. After cooling to -30°C , the bright yellow product was collected on a frit, washed with pentane and dried under reduced pressure. The yield was 0.3168 g (37.4%). ^1H NMR (C_6D_6): δ 3.64 (s, 3H), 1.97 (s, 6H), 1.95 (s, 6H), 0.21 (s, 6H). ^{13}C NMR (C_6D_6): δ 140.5, 135.5, 103.0, 41.8, 15.5, 12.3, 0.6.

Polymerization

The polymerization procedure of Example 55 was followed using 10 micromoles of the above complex. The polymer yield was 30.2 g.

Example 64 Terpolymer Polymerization

Mixtures of ethylene, styrene and another additional polymerizable monomer were polymerized using (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitanium dichloride complex and MAO cocatalyst in an amount to provide an atomic ratio Al/Ti of 1000:1. Reaction conditions and results are contained in Table V.

Table V

In each case the cocatalyst was methylaluminoxane and the metal complex was (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)titanium dichloride.

Run	mg (complex)	T (°C)	Solvent (ml) ^a	Ethylene kPa (psig)	Styrene (ml)	Olefin(g)	Time (hr)	Yield (g)	mol% Styrene	mol% Olefin	M _w	M _w /M _n
1	1.8	90	I (670)	1615 (220)	38	butene (19)	0.5	51	2.3	6.6	141,000	2.9
2	1.9	90	I (630)	"	76	butene (9)	0.5	46	3.4	4.6	166,000	2.4
3	1.9	90	I (455)	"	250	butene (5)	0.5	70	7.2	3.2	163,000	2.4
4	2.2	90	T (40)	1240 (180)	133	Vinyl- BCB (1.5) ^b	2.0	37	22.4	<1	39,000	1.7

a. I = mixed alkane solvent, T = toluene

b. Vinyl-BCB = vinyl benzocyclobutane

Example 65 Slurry Polymerization

The following example demonstrates the use of a catalyst of the present invention under slurry conditions. The procedure of Examples 6-27 was substantially followed, excepting that the reaction was run under conditions where the polymer was insoluble in the reaction medium and precipitated from the reaction mixture as it formed. The temperature was 70°C, 10 mL of octene, 1190 mL of mixed alkane solvent, and 5 mL of 15 percent MAO in toluene (1280 Al:Ti) were used. After 20 minutes, the reactor was drained to give 4.6 g of polymer. Additional solvent was added to the reactor and heated to 170°C to remove the polymer that had formed long filaments and wound around the stirrer. The melt index was 0.28.

Example 66 Preparation of (Tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)-silanetitanium(III) chloride

In the drybox, 0.24 g of $\text{TiCl}_3(\text{THF})_3$ and 0.33 g of $\text{Me}_4\text{C}_5\text{SiMe}_2\text{N-t-BuMg}_2\text{Cl}_2(\text{THF})_2$ were mixed. 15 mL Of THF was added, resulting in a deep purple color. After 30 minutes the volatile materials were removed under reduced pressure to leave a dark solid. Toluene (15 mL) was added, the solution filtered, and the toluene was removed under reduced pressure to leave a red-purple powder, 0.22 g.

Polymerization

The polymerization procedure of Example 55 was followed using 10 micromoles of the above complex. The polymer yield was 55.1 g, melt index = 1.71.

Example 67

The polymerization procedure of Example 55 was followed using 10 micromoles of (tert-butylamido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silanetitanium dichloride. The polymer yield was 76.4 g, Mw = 56,700, Mw/Mn = 4.5, density = 0.8871, melt index (I_2) = 10.13.

Example 68

The polymerization procedure of Example 67 was substantially followed except that the temperature was 80°C, the amount of catalyst used was 2.5 micromoles, the amount of 1-octene used was 250 mL, and the amount of mixed alkane solvent used was 950 mL. The reaction was allowed to proceed for 1 hour. The polymer yield was 51.1 g. The melt index was 0.11.

Comparative 1

The polymerization procedure of Example 67 was followed except that the catalyst was pentamethylcyclopentadienyltitanium trichloride. The polymer yield was 4.6 g.

Comparative 2

The polymerization procedure of Example 67 was followed except that the catalyst was pentamethyl- η^5 -cyclopentadienyltitanium tert-butylamino dichloride (^1H NMR (C_6D_6): δ 2.07 (s, 1H), 1.88 (s, 15H), 1.35 (s, 9H). ^{13}C NMR (C_6D_6): δ 61.0, 31.3, 12.6). The polymer yield was 2.0 g.

Comparative 3

The polymerization procedure of Example 67 was followed except that the catalyst was bis-(tert-butylamido)dimethylsilanetitanium dichloride. No polymer was observed after 10 minutes of reaction.

Comparative 4

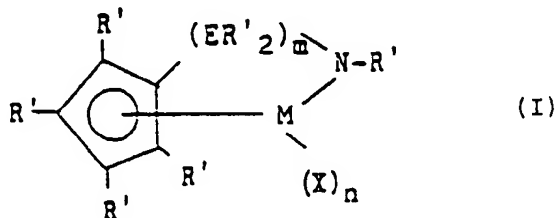
The polymerization procedure of Example 67 was followed except that the catalyst was dicyclopentadienylzirconium dichloride. The polymer yield was 109.0 g, Mw = 16,300, Mw/Mn = 3.63, melt index ASTM D-1238 Procedure A, condition E, I_2 , was greater than 1,000 indicating a very low molecular weight polymer.

Comparative 5

The polymerization procedure of Example 67 was followed except that the catalyst was dicyclopentadienyltitanium dichloride. The polymer yield was 7.3 g, melt index, ASTM D-1238 Procedure A, condition E, I_2 , was greater than 1,000 indicating a very low molecular weight polymer.

Claims

1. A metal coordination complex corresponding to the Formula I:



wherein:

- M is titanium bound in an η^5 bonding mode to the cyclopentadienyl group;
 R' each occurrence is hydrogen or a moiety selected from silyl, alkyl, aryl, or combinations thereof having up to 10 carbon or silicon atoms;
 E is silicon;
 X each occurrence is halo, alkyl, aryl, or alkoxy of up to 10 carbons;
 m is 1 or 2; and
 n is 1 or 2 depending on the valence of M.
2. A metal coordination complex as claimed in Claim 1, wherein each R' is hydrogen, C_{1-6} alkyl, norbornyl, benzyl or phenyl; and X is chloro, bromo, iodo, C_{1-6} alkyl, norbornyl, benzyl or phenyl.
 3. A metal coordination complex as claimed in Claim 2, wherein X is methyl.
 4. A metal coordination complex as claimed in Claim 2, wherein X is benzyl.
 5. A metal coordination complex as claimed in any one of the preceding claims, wherein NR' is tert. butylamido.
 6. A metal coordination complex as claimed in any one of Claims 1 to 4, wherein NR' is phenylamido.
 7. A metal coordination complex as claimed in Claim 1, wherein n is 1.
 8. A metal coordination complex as claimed in Claim 1, wherein n is 2.
 9. A metal coordination complex as claimed in Claim 1, wherein m is 1.
 10. A metal coordination complex as claimed in Claim 1, wherein m is 2.
 11. 1-(Tert-butylamido)-2-(tetramethyl- η^5 -cyclopentadienyl)-1,1,2,2-tetramethyldisilane titanium dichloride.
 12. A metal coordination complex selected from:
 - (tert-butylamido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silane titanium dichloride;
 - (benzylamido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silane titanium dichloride;
 - (2-methoxyphenylamido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silane titanium dichloride;
 - ((2,6-di(1-methylethyl)phenyl)amido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silane titanium dichloride;

(4-methoxyphenylamido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silane titanium dichloride;
 (4-methylphenylamido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silane titanium dichloride;
 (phenylamido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silane titanium dichloride;
 (tert-butylamido)dimethyl-(η^5 -cyclopentadienyl)silane-titanium dichloride;
 (anilido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)-silane titanium dichloride;
 (methylamido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silane titanium dichloride; and
 (tert-butylamido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silane titanium (III) chloride.

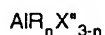
13. A catalyst useful in addition polymerizations comprising

- a) a metal coordination complex as claimed in any one of Claims 1 to 12, and
 b) an activating cocatalyst.

14. A catalyst as claimed in Claim 13, wherein said activating cocatalyst comprises an aluminum compound.

15. A catalyst as claimed in Claim 14, wherein said aluminum compound is an alkylaluminum compound, aluminum alkyl, aluminum halide, or aluminum alkylhalide.

16. A catalyst as claimed in Claim 14, wherein the activating cocatalyst is selected from alkylaluminum compounds, and compounds corresponding to the formula:



wherein:

R is each occurrence C_{1-10} alkyl or aralkyl;
 X is halogen; and
 n is 1, 2 or 3.

17. A process for preparing a metal coordination complex corresponding to the Formula I as defined in Claims 1 comprising contacting a metal compound of the formula MX_{n+2} or a coordinated adduct thereof with a dianionic salt compound corresponding to the Formula II or III:



or



wherein:

Cp^* is the cyclopentadienyl or substituted cyclopentadienyl group $\text{C}_5\text{R}'_4$ of Formula I;
 L is a metal of Group 1 or 2 of the Periodic Table of the Elements,
 x and y are either 1 or 2 and the product of x and y equals 2,
 X is fluoro, bromo, chloro or iodo, and
 n, E, M, m, R' and X are as defined in Claim 1,

in an inert solvent.

18. A process for preparing a metal coordination complex corresponding to the Formula I as defined in Claim 1 comprising

- (a) contacting a metal compound of the formula MX_{n+1} or a coordinated adduct thereof with a dianionic salt compound corresponding to the Formula II or III:



or



wherein:

Cp* is the cyclopentadienyl or substituted cyclopentadienyl group C₅R'₄ of Formula I;

L is a metal of Group 1 or 2 of the Periodic Table of the Elements,

x and y are either 1 or 2 and the product of x and y equals 2,

X* is fluoro, bromo, chloro or iodo, and

n, E, M, m, R' and X are as defined in Claim 1,

in an inert solvent, and,

(b) contacting the product of (a) with a noninterfering oxidizing agent to raise the oxidation state of the metal.

19. A process as claimed in Claim 17 or Claim 18, wherein the solvent is selected from cyclohexane, tetrahydrofuran, methylcyclohexane, pentane, hexane, heptane, benzene, toluene, xylene and ethylbenzene.

20. A process as claimed in Claim 19, wherein the solvent is toluene or tetrahydrofuran.

21. A process for preparing a catalyst as claimed in Claim 13, comprising contacting a complex as defined in any one of Claims 1 to 12 with an activating cocatalyst.

22. A process for preparing a catalyst as claimed in Claim 21, wherein the activating cocatalyst is as defined in any one of Claims 14 to 16.

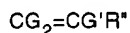
23. An addition polymerization process for preparing a polymer by contacting one or more addition polymerizable monomers with a catalyst under addition polymerization conditions characterized in that the catalyst is as defined in any one of Claims 13 to 16.

24. A process as claimed in Claim 23, wherein the addition polymerizable monomers are selected from ethylenically unsaturated monomers, acetylenic compounds, conjugated or nonconjugated dienes, and polyenes having from 2 to 20 carbons.

25. A process as claimed in Claim 24, wherein an alpha olefin is copolymerized with a vinylidene aromatic or hindered aliphatic vinyl monomers.

26. A process as claimed in Claim 25, wherein ethylene is copolymerized with styrene or vinylcyclohexene.

27. A process for preparing a copolymer of a hindered aliphatic vinylidene monomer corresponding to the formula:



wherein R'' is an sterically bulky, aliphatic substituent of up to 20 carbons, G independently each occurrence is hydrogen or methyl, and G' independently each occurrence is hydrogen or methyl or alternatively G' and R'' together form a ring system

and an alpha-olefin wherein the hindered aliphatic vinylidene monomer is contacted with the alpha-olefin under polymerization conditions in the presence of a catalyst comprising

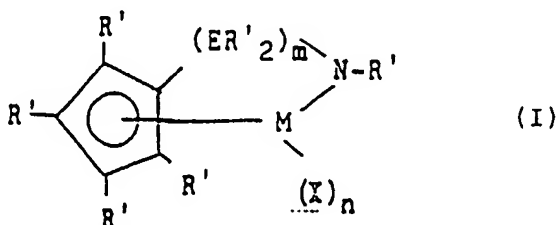
a) a metal coordination complex as defined in any one of Claims 1 to 12

b) an activating cocatalyst.

28. A process as claimed in Claim 27, wherein the activating cocatalyst is as defined in any one of Claims 14 to 16.
29. A process as claimed in Claim 27 or Claim 28, wherein the hindered aliphatic vinylidene monomer is one in which the carbon atoms bearing ethylenic unsaturation is tertiary or quaternary substituted.
30. A process as claimed in Claim 29, wherein said carbon atom is substituted by a cyclic aliphatic group.
31. A process as claimed in Claim 30, wherein the hindered aliphatic vinylidene monomer is 1-, 3- or 4-vinylcyclohexene or 5-ethylidene-2-norbornene.
32. A heterogeneous supported catalyst comprising a metal coordination complex corresponding to the Formula I as defined in Claim 1 and an activating cocatalyst.
33. A heterogeneous supported catalyst as claimed in Claim 32, wherein the support is selected from alumina, $MgCl_2$ and silica.

Patentansprüche

1. Metallkoordinationskomplex entsprechend der Formel I:

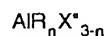


in der,

M Titan ist, das über eine η^5 -Bindung an die Cyclopentadienylgruppe gebunden ist,
 R' bei jedem Auftreten Wasserstoff oder eine Einheit, ausgewählt aus Silyl, Alkyl, Aryl oder Kombinationen davon mit bis zu 10 Kohlenstoff- oder Siliciumatomen ist,
 E Silicium ist,
 X bei jedem Auftreten Halogen, Alkyl, Aryl oder Alkoxy mit bis zu 10 Kohlenstoffatomen ist,
 m = 1 oder 2 ist und n = 1 oder 2 in Abhängigkeit von der Valenz von M ist.

2. Metallkoordinationskomplex nach Anspruch 1, worin jedes R' Wasserstoff, C_{1-6} -Alkyl, Norbornyl, Benzyl oder Phenyl ist und x Chlor, Brom, Iod, C_{1-6} -Alkyl, Norbornyl, Benzyl oder Phenyl ist.
3. Metallkoordinationskomplex nach Anspruch 2, worin X Methyl ist.
4. Metallkoordinationskomplex nach Anspruch 2, worin X Benzyl ist.
5. Metallkoordinationskomplex nach einem der vorstehenden Ansprüche, in dem NR' Tertiärbutylamido ist.
6. Metallkoordinationskomplex nach einem der Ansprüche 1-4, worin NR' Phenylamido ist.
7. Metallkoordinationskomplex nach Anspruch 1, worin n = 1 ist.
8. Metallkoordinationskomplex nach Anspruch 1, worin n = 2 ist.
9. Metallkoordinationskomplex nach Anspruch 1, worin m = 1 ist.
10. Metallkoordinationskomplex nach Anspruch 1, worin m = 2 ist.

11. 1-(tert-Butylamido)-2-(tetramethyl- η^5 -cyclopentadienyl)-1,1,2,2-tetramethyldisilantitandichlorid.
12. Metallkoordinationskomplex ausgewählt aus (tert-Butylamido)dimethyl-(tetramethyl-(η^5 -cyclopentadienyl)silantitandichlorid,
- 5 (Benzylamido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silantitandichlorid,
(2-Hethoxyphenylamido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silantitandichlorid,
((2,6-Di(1-methylethyl)phenyl)amido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silantitandichlorid,
10 (4-Methoxyphenylamido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silantitandichlorid, (4-Methylphenylamido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silantitandichlorid, (Phenylamido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silantitandichlorid,
(tert-Butylamido)dimethyl-(η^5 -cyclopentadienyl)silantitandichlorid,
(Anilido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silantitandichlorid,
15 (Methylamido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silantitandichlorid, und
(tert-Butylamido)dimethyl-(tetramethyl- η^5 -cyclopentadienyl)silantitan(III)-chlorid.
13. Katalysator, der bei Additionspolymerisation verwendet werden kann, umfassend
- a) einen Metallkoordinationskomplex nach einem der Ansprüche 1-12 und
20 b) einen aktivierenden Cokatalysator.
14. Katalysator nach Anspruch 13, worin der aktivierende Cokatalysator eine Aluminiumverbindung enthält.
15. Katalysator nach Anspruch 14, worin die Aluminiumverbindung ein Alkylaluminoxan, Aluminiummalkyl, Aluminiumhalogenid oder Aluminiummalkylhalogenid ist.
- 25 16. Katalysator nach Anspruch 14, worin der aktivierende Cokatalysator ausgewählt ist aus Alkylaluminooxanen und Verbindungen entsprechend der Formel:



in der,

35 R bei jedem auftreten C_{1-10} -Alkyl oder Aralkyl ist,
 X^* Halogen und
 $n = 1, 2$ oder 3 ist.

17. Verfahren zur Herstellung eines Metallkoordinationskomplexes entsprechend der Formel I, wie in Anspruch 1 definiert, umfassend Inberührungbringen einer Metallverbindung der Formel MX_{n+2} oder eines koordinierten Addukts davon mit einer dianionischen Salzverbindung entsprechend der Formel II oder III:



45 oder



50 worin

CP* die Cyclopentadienyl- oder substituierte Cyclopentadienylgruppe $\text{C}_5\text{R}'_4$ der Formel I ist,
L ein Metall der Gruppe 1 oder 2 des Periodensystems der Elemente ist,
55 x und y entweder 1 oder 2 sind und das Produkt von x und y 2 entspricht,
 X^* Fluor, Brom, Chlor oder Iod ist und
n, E, M, m, R' und X wie in Anspruch 1 definiert sind,

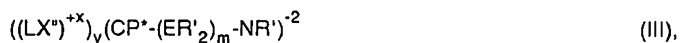
in einem inerten Lösungsmittel.

18. Verfahren zur Herstellung eines Metallkoordinationskomplexes entsprechend der Formel I, wie in Anspruch 1 definiert, umfassend

(a) Inberührungbringen einer Metallverbindung der Formel MX_{n+1} oder eines koordinierten Addukts davon mit einer dianionischen Salzverbindung entsprechend der Formel II oder III:



oder



worin

CP* die Cyclopentadienyl- oder substituierte Cyclopentadienylgruppe $C_5R'_4$ der Formel I ist,
L ein Metall der Gruppe 1 oder 2 des Periodensystems der Elemente ist,
x und y entweder 1 oder 2 sind und das Produkt von x und y 2 entspricht,
X* Fluor, Brom, Chlor oder Iod ist und
n, E, M, m, R' und X wie in Anspruch 1 definiert sind,

in einem inerten Lösungsmittel und

(b) Inberührungbringen des Produktes aus (a) mit einem nicht wechselwirkenden Oxidationsmittel, um die Oxidationsstufe des Metalls zu erhöhen.

19. Verfahren nach Anspruch 17 oder 18, worin das Lösungsmittel ausgewählt ist aus Cyclohexan, Tetrahydrofuran, Methylcyclohexan, Pentan, Hexan, Heptan, Benzol, Toluol, Xylol und Ethylbenzol.

20. Verfahren nach Anspruch 19, worin das Lösungsmittel Toluol oder Tetrahydrofuran ist.

21. Verfahren zur Herstellung eines Katalysators nach Anspruch 13, umfassend Inberührungbringen eines Komplexes wie in einem der Ansprüche 1-12 definiert mit einem aktivierenden Cokatalysator.

22. Verfahren zur Herstellung eines Katalysators nach Anspruch 21, worin der aktivierende Cokatalysator wie in einem der Ansprüche 14-16 definiert ist.

23. Additionspolymerisationsverfahren zur Herstellung eines Polymers durch Inberührungbringen von einem oder mehreren additionspolymerisierbaren Monomeren mit einem Katalysator unter Additionspolymerisationsbedingungen,

dadurch gekennzeichnet,

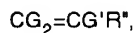
daß der Katalysator wie in einem der Ansprüche 13-16 definiert ist.

24. Verfahren nach Anspruch 23, worin die additionspolymerisierbaren Monomeren ausgewählt sind aus ethylenisch ungesättigten Monomeren, acetylenischen Verbindungen, konjugierten oder nichtkonjugierten Dienen und Polymeren mit 2-20 Kohlenstoffatomen.

25. Verfahren nach Anspruch 24, worin ein alpha-Olefin mit einem vinylidenaromatischen oder gehinderten aliphatischen Vinylmonomeren copolymerisiert wird.

26. Verfahren nach Anspruch 25, worin Ethylen mit Styrol oder Vinylcyclohexen polymerisiert wird.

27. Verfahren zur Herstellung eines Copolymers aus einem gehinderten aliphatischen Vinylidenmonomer entsprechend der Formel



worin R^* ein sterisch anspruchsvoller, aliphatischer Substituent mit bis zu 20 Kohlenstoffatomen ist, G unabhängig bei jedem Auftreten Wasserstoff oder Methyl ist und G' unabhängig bei jedem auftreten Wasserstoff oder Methyl ist oder alternativ hierzu G' und R^* zusammen ein Ringsystem bilden, und einem alpha-Olefin, worin das gehinderte aliphatische Vinylidenmonomer mit dem alpha-Olefin unter Polymerisationsbedingungen in Gegenwart eines Katalysators, enthaltend

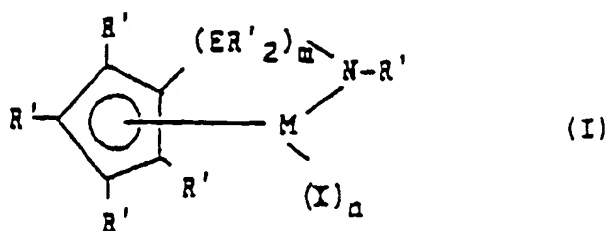
- (a) einen Metallkoordinationskomplex wie in einem der Ansprüche 1-12 definiert und
(b) einen aktivierenden Kokatalysator,

in Berührung gebracht wird.

28. Verfahren nach Anspruch 27, worin der aktivierende Kokatalysator wie in einem der Ansprüche 14-16 definiert ist.
29. Verfahren nach Anspruch 27 oder 28, worin das gehinderte aliphatische Vinylidenmonomer eines ist, in welchem die Kohlenstoffatome, die die ethylenische Unsättigung tragen, tertiär oder quaternär substituiert sind.
30. Verfahren nach Anspruch 29, worin das Kohlenstoffatom mit einer cyclischen aliphatischen Gruppe substituiert ist.
31. Verfahren nach Anspruch 30, worin das gehinderte aliphatische Vinylidenmonomer 1-, 3- oder 4-Vinylcyclohexen oder 5-Ethyliden-2-norbornen ist.
32. Heterogener Katalysator auf einem Träger, enthaltend einen Metallkoordinationskomplex entsprechend der Formel I, wie in Anspruch 1 definiert, und einen aktivierenden Kokatalysator.
33. Heterogener Katalysator auf einem Träger nach Anspruch 32, worin der Träger ausgewählt ist aus Aluminiumoxid, $HgCl_2$ und Siliciumdioxid.

Revendications

1. Complexe métallique de coordination correspondant à la formule I:



dans laquelle:

M est le titane lié par une liaison en η^5 au groupe cyclopentadiényle;
dans chaque cas R' représente un hydrogène ou un radical choisi parmi les groupes silyle, alkyle, aryle ou leurs combinaisons possédant jusqu'à 10 atomes de carbone ou de silicium;
E est le silicium;
dans chaque cas X est un radical halogéno, alkyle, aryle, ou alcoxy comprenant jusqu'à 10 atomes de carbone;
m vaut 1 ou 2; et
n vaut 1 ou 2 en fonction de la valence de M.

2. Complexe métallique de coordination selon la revendication 1, dans lequel chaque R' représente un hydrogène, un groupe alkyle en C_1 à C_6 , norbornyle, benzyle, ou phényle; et X est un groupe chloro, bromo, iodo, alkyle en C_1 à C_6 , norbornyle, benzyle ou phényle.

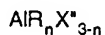
3. Complexe métallique de coordination selon la revendication 2, dans lequel X est un groupe méthyle.
4. Complexe métallique de coordination selon la revendication 2, dans lequel X est un groupe benzyle.
5. Complexe métallique de coordination selon l'une des revendications précédentes, dans lequel NR' est un radical t-butylamido.
6. Complexe métallique de coordination selon l'une des revendications 1 à 4, dans lequel NR' est un radical phénylamido.
7. Complexe métallique de coordination selon la revendication 1, dans lequel n vaut 1.
8. Complexe métallique de coordination selon la revendication 1, dans lequel n vaut 2.
9. Complexe métallique de coordination selon la revendication 1, dans lequel m vaut 1.
10. Complexe métallique de coordination selon la revendication 1, dans lequel m vaut 2.
11. Dichlorure de 1-(t-butylamido)-2-(tétraméthyl- η^5 -cyclopentadiényl)-1,1,2,2-tétraméthylsilane-titane
12. Complexe métallique de coordination choisi parmi:

le dichlorure de (t-butylamido)diméthyl-(tétraméthyl- η^5 -cyclopentadiényl)silane-titane;
 le dichlorure de (benzylamido)diméthyl-(tétraméthyl- η^5 -cyclopentadiényl)silane-titane;
 le dichlorure de (2-méthoxyphénylamido)diméthyl-(tétraméthyl- η^5 -cyclopentadiényl)silane-titane;
 le dichlorure de ((2,6-di(1-méthyléthyl)phényl)-amido)diméthyl-(tétraméthyl- η^5 -cyclopentadiényl)silane-titane;
 le dichlorure de (4-méthoxyphénylamido)diméthyl-(tétraméthyl- η^5 -cyclopentadiényl)silane-titane;
 le dichlorure de (4-méthylphénylamido)diméthyl-(tétraméthyl- η^5 -cyclopentadiényl)silane-titane;
 le dichlorure de (phénylamido)diméthyl-(tétraméthyl- η^5 -cyclopentadiényl)silane-titane;
 le dichlorure de (t-butylamido)diméthyl-(η^5 -cyclopentadiényl)silane-titane;
 le dichlorure de (anilido)diméthyl-(tétraméthyl- η^5 -cyclopentadiényl)silane-titane;
 le dichlorure de (méthylamido)diméthyl-(tétraméthyl- η^5 -cyclopentadiényl)silane-titane; et
 le chlorure de (t-butylamido)diméthyl-(tétraméthyl- η^5 -cyclopentadiényl)silane-titane (III).

13. Catalyseur utilisable dans les polymérisations par addition comprenant

a) un complexe métallique de coordination selon l'une des revendications 1 à 12, et
 b) un cocatalyseur d'activation.

14. Catalyseur selon la revendication 13, dans lequel ledit cocatalyseur d'activation comprend un composé d'aluminium.
15. Catalyseur selon la revendication 14, dans lequel ledit composé d'aluminium est un alkylaluminosilane, un alkylaluminium, un halogénure d'aluminium, ou un alkylhalogénure d'aluminium.
16. Catalyseur selon la revendication 14, dans lequel ledit le cocatalyseur d'activation est choisi parmi les alkylaluminosilanes, et les composés correspondant à la formule:



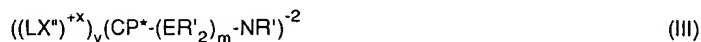
dans laquelle:
 dans chaque cas

R représente un groupe alkyle ou aralkyle en C_1 à C_{10} ;
 X^* est un halogène; et
 n vaut 1, 2 ou 3.

17. Procédé pour la préparation d'un complexe métallique de coordination correspondant à la formule I telle que définie dans la revendication 1, comprenant les étapes consistant à mettre un composé métallique de formule MX_{n+2} ou un produit d'addition de coordination de celui-ci en contact avec un sel dianionique correspondant aux formules II ou III:



ou



dans lesquelles:

Cp^* est le groupe cyclopentadiényle ou cyclopentadiényle substitué $C_5R'_4$ de formule I,

L est un métal des Groupes 1 ou 2 du Tableau Périodique des Eléments,

x et y valent soit 1 soit 2 et le produit de x par y est égal à 2, et

X^* est un radical fluoro, chloro, bromo ou iodo,

n, E, M, m, R' et X sont tels que définis dans la revendication 1,

dans un solvant inerte.

18. Procédé pour la préparation d'un complexe métallique de coordination correspondant à la formule I telle que définie dans la revendication 1, comprenant les étapes consistant:

(a) à mettre un composé métallique de formule MX_{n+1} ou un produit d'addition de coordination de celui-ci en contact avec un sel dianionique correspondant aux formules II ou III:



ou



dans lesquelles:

Cp^* est le groupe cyclopentadiényle ou cyclopentadiényle substitué $C_5R'_4$ de formule I,

L est un métal des Groupes 1 ou 2 du Tableau Périodique des Eléments,

x et y valent soit 1 soit 2 et le produit de x par y est égal à 2, et

X^* est un radical fluoro, chloro, bromo ou iodo,

n, E, M, m, R' et X sont tels que définis dans la revendication 1,

dans un solvant inerte, et,

(b) à mettre le produit de (a) en contact avec un agent oxydant non interférant pour élever l'état d'oxydation du métal.

19. Procédé selon l'une des revendications 17 ou 18, dans lequel le solvant est choisi dans le groupe formé par le cyclohexane, le tétrahydrofurane, le méthylcyclohexane, le pentane, l'hexane, l'heptane, le benzène, le toluène, le xylène et l'éthylbenzène.

20. Procédé selon la revendication 19, dans lequel le solvant est le toluène ou le tétrahydrofurane.

21. Procédé de préparation d'un catalyseur selon la revendication 13, comprenant les étapes consistant à mettre un complexe tel que défini dans l'une des revendications 1 à 12 en contact avec un cocatalyseur d'activation.

22. Procédé de préparation d'un catalyseur selon la revendication 21, dans lequel le cocatalyseur d'activation est tel que défini dans l'une des revendications 14 à 16.

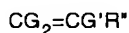
23. Procédé de polymérisation par addition pour préparer un polymère en mettant en contact un ou plusieurs monomères polymérisables par addition avec un catalyseur dans des conditions de polymérisation par addition caractérisé en ce que le catalyseur est tel que défini dans l'une des revendications 13 à 16.

24. Procédé selon la revendication 23, dans lequel les monomères polymérisables par addition sont choisis dans le groupe formé par les monomères éthyléniquement insaturés, les composés acétyléniques, les diènes conjugués ou non conjugués, les polyènes possédant de 2 à 20 atomes de carbone.

25. Procédé selon la revendication 24, dans lequel une alpha-oléfine est copolymérisée avec un monomère vinylidène aromatique ou vinylique aliphatique encombré.

26. Procédé selon la revendication 25, dans lequel l'éthylène est copolymérisé avec le styrène ou le vinylcyclohexène.

27. Procédé pour la préparation d'un copolymère d'un monomère vinylidène aliphatique encombré correspondant à la formule:



dans laquelle R'' est un substituant aliphatique stériquement volumineux ayant jusqu'à 20 atomes de carbone, G représentant indépendamment dans chaque cas un hydrogène ou un groupe méthyle, et G' représentant indépendamment dans chaque cas un hydrogène ou un groupe méthyle ou en variante G' et R'' forment ensemble un système cyclique et une alpha-oléfine dans laquelle le monomère vinylidène aliphatique encombré est mis en contact avec l'alpha-oléfine dans des conditions de polymérisation en présence d'un catalyseur comprenant

- a) un complexe métallique de coordination tel que défini dans l'une des revendications 1 à 12
- b) un cocatalyseur d'activation.

28. Procédé selon la revendication 27, dans lequel le cocatalyseur d'activation est tel que défini dans l'une des revendications 14 à 16.

29. Procédé selon l'une des revendications 27 ou 28, dans lequel le monomère vinylidène aliphatique encombré est un monomère dans lequel l'atome de carbone portant l'insaturation éthylénique est substitué de manière tertiaire ou quaternaire.

30. Procédé selon la revendication 29, dans lequel ledit atome de carbone est substitué par un groupe aliphatique cyclique.

31. Procédé selon la revendication 30, dans lequel le monomère vinylidène aliphatique encombré est le 1-, le 3- ou le 4-vinylcyclohexène ou le 5-éthylidène-2-norbornène.

32. Catalyseur hétérogène supporté comprenant un complexe métallique de coordination correspondant à la formule I telle que définie dans la revendication 1 et un cocatalyseur d'activation.

33. Catalyseur hétérogène supporté selon la revendication 32, dans lequel le support est choisi parmi l'alumine, $MgCl_2$, et la silice.

FIG.1

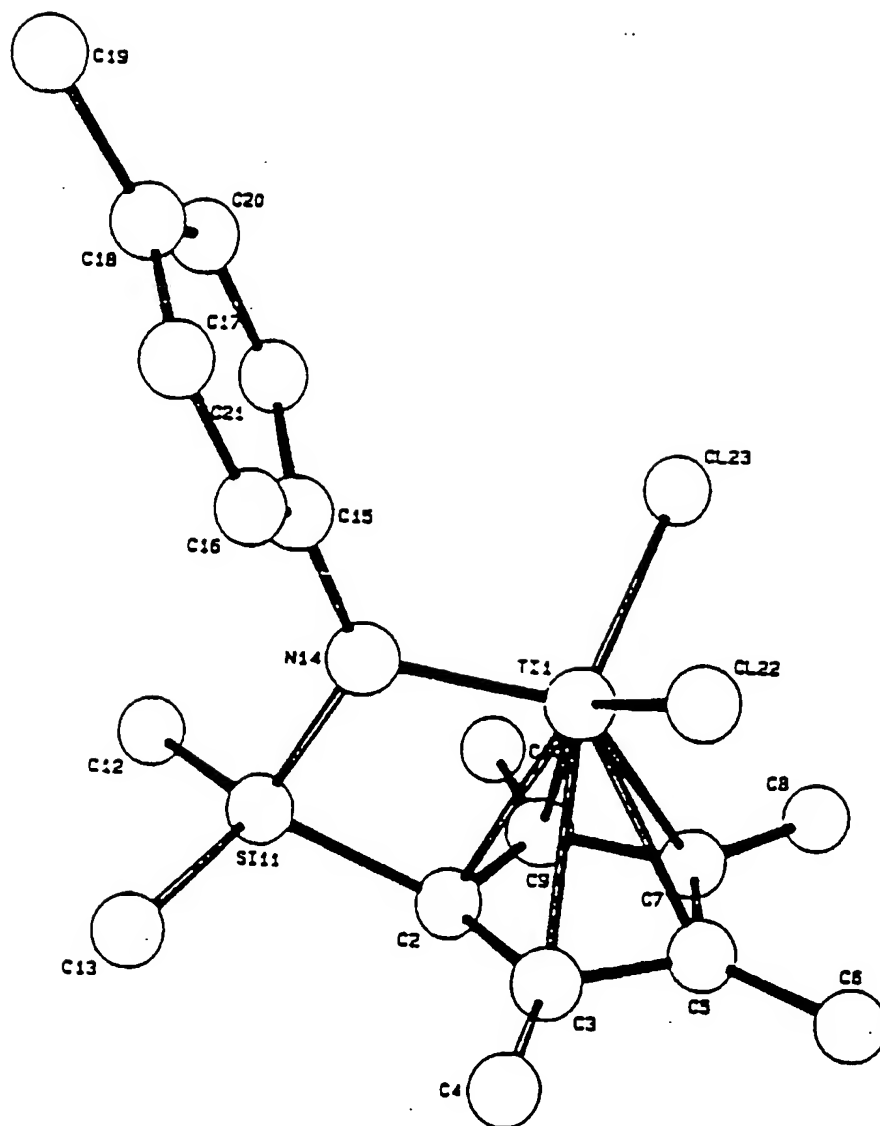


FIG.2

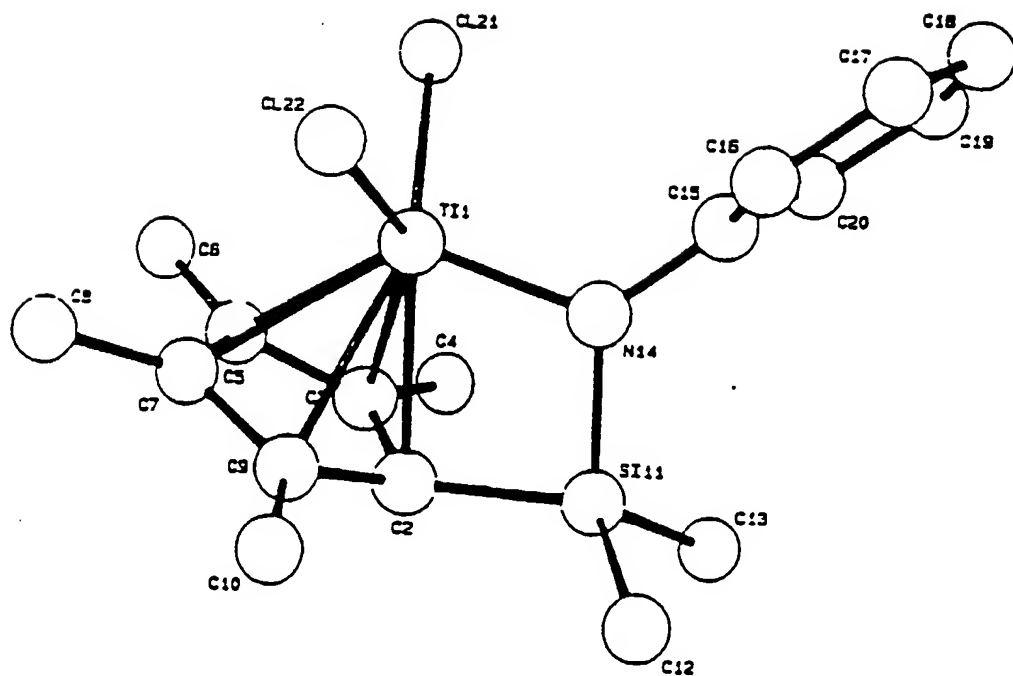


FIG. 3

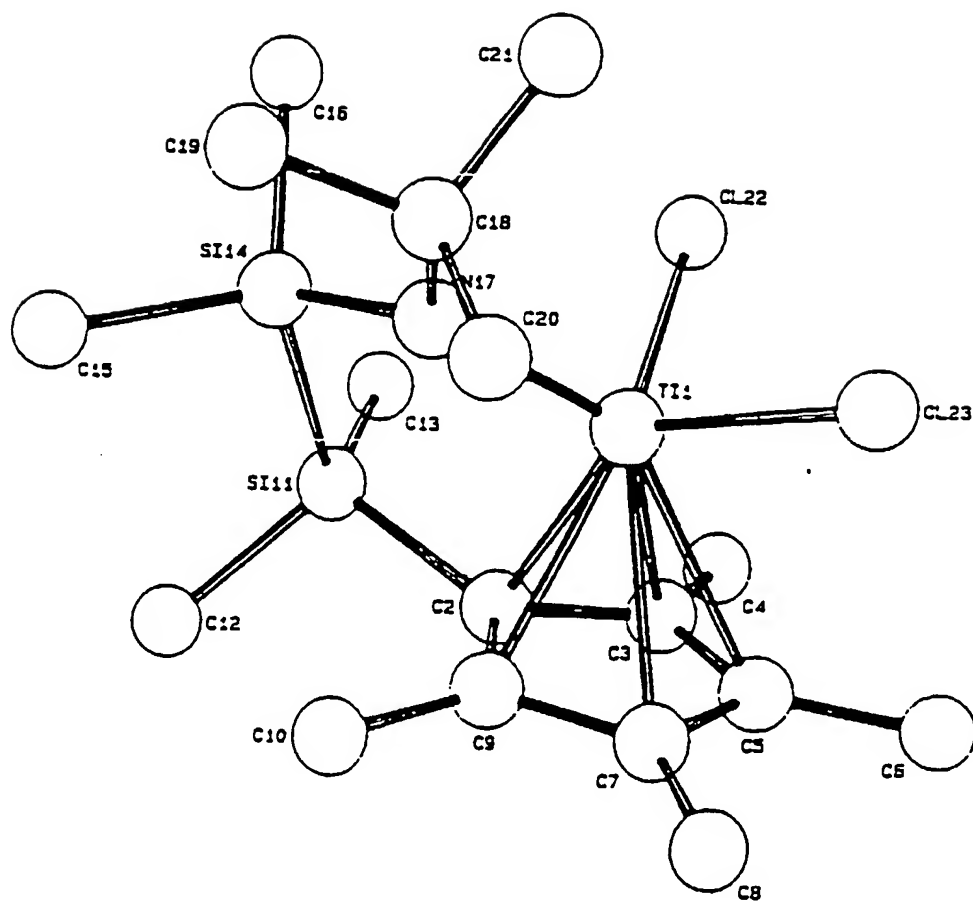


FIG. 4

Ethylene / Styrene Pseudo-random Copolymer 1.4 Mole % Styrene, 15% Tail-to-Tail

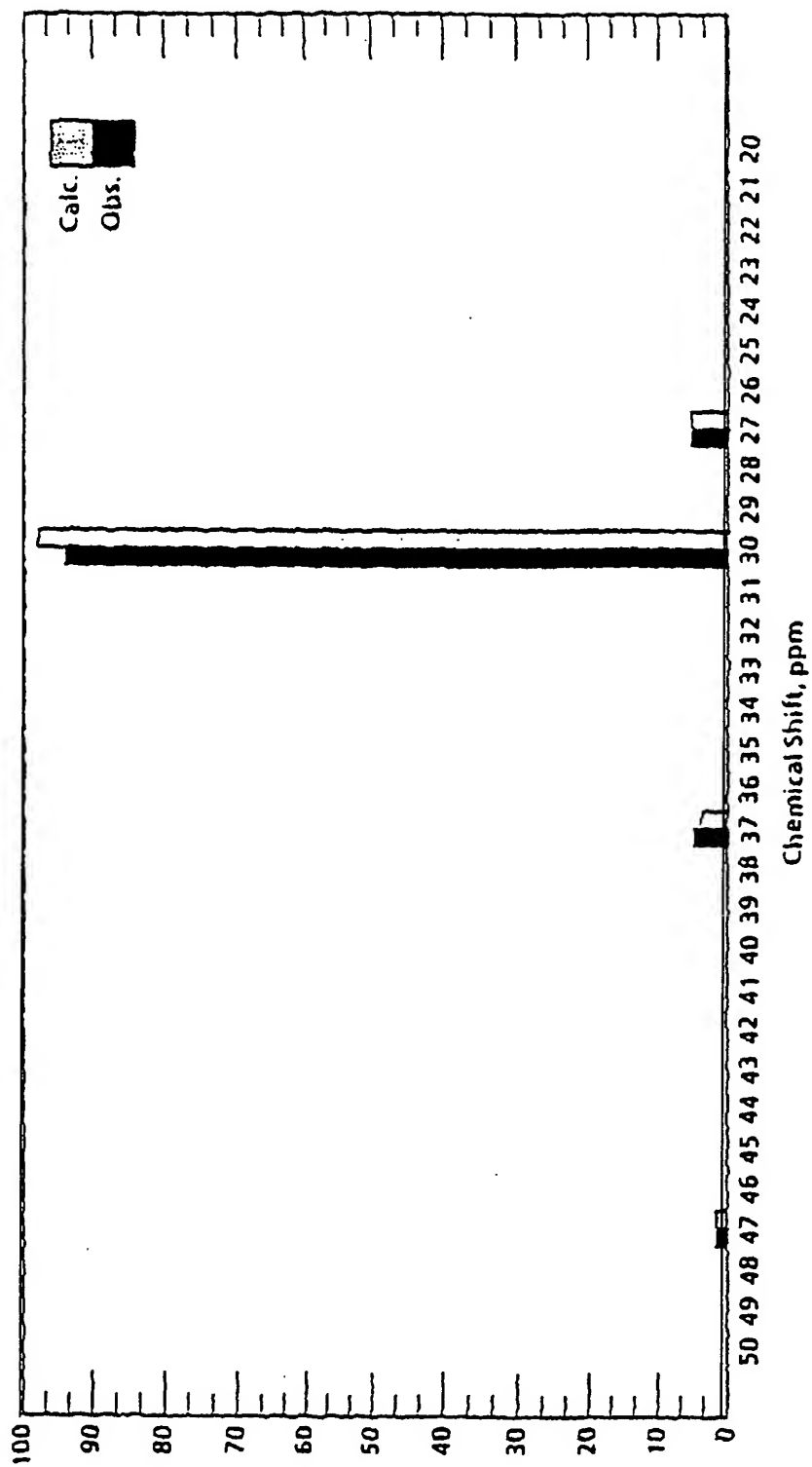


FIG. 5

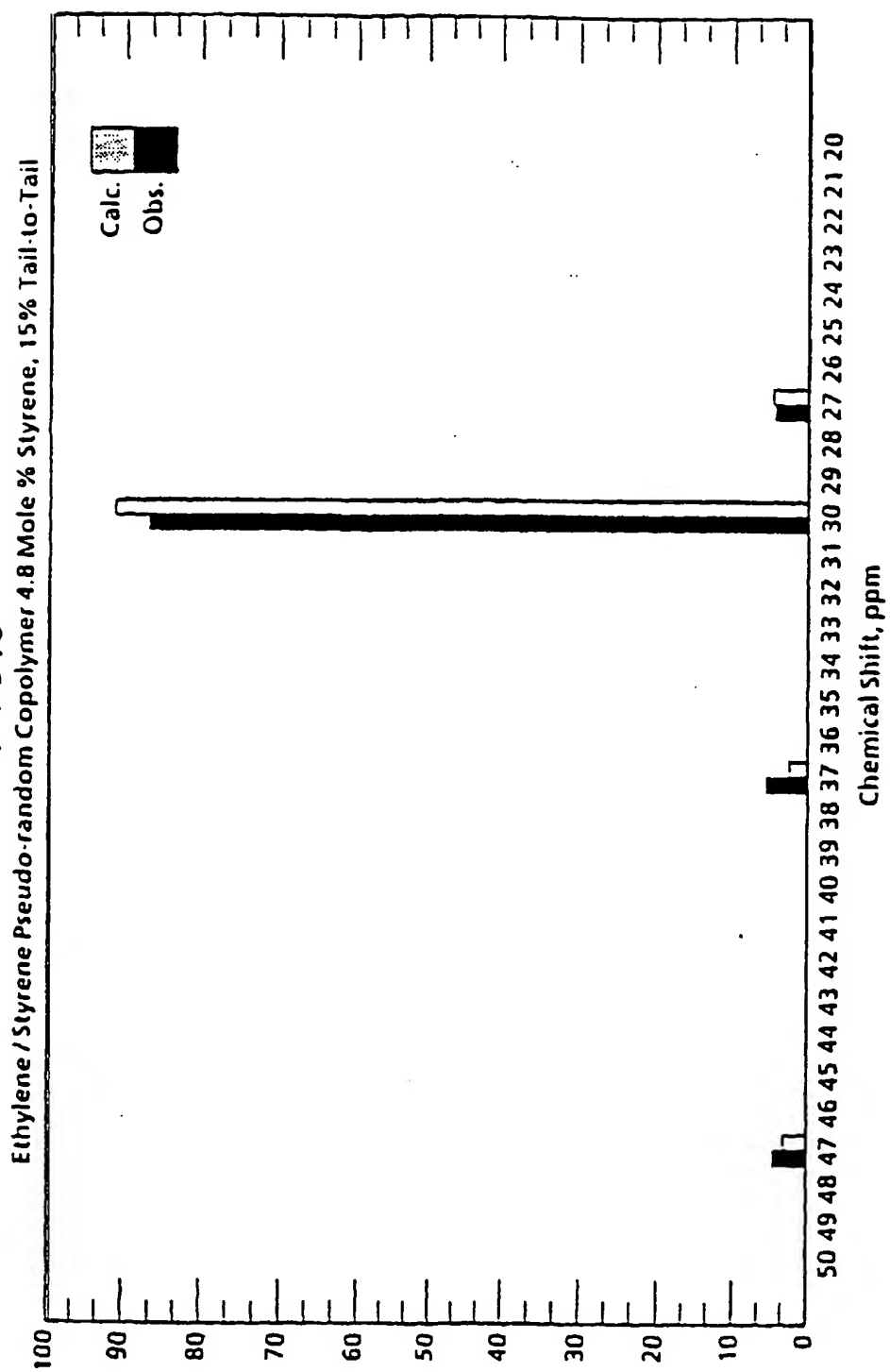


FIG.6

Ethylene / Styrene Pseudo-random Copolymer 9.0 Mole % Styrene, 15% Tail-to-Tail

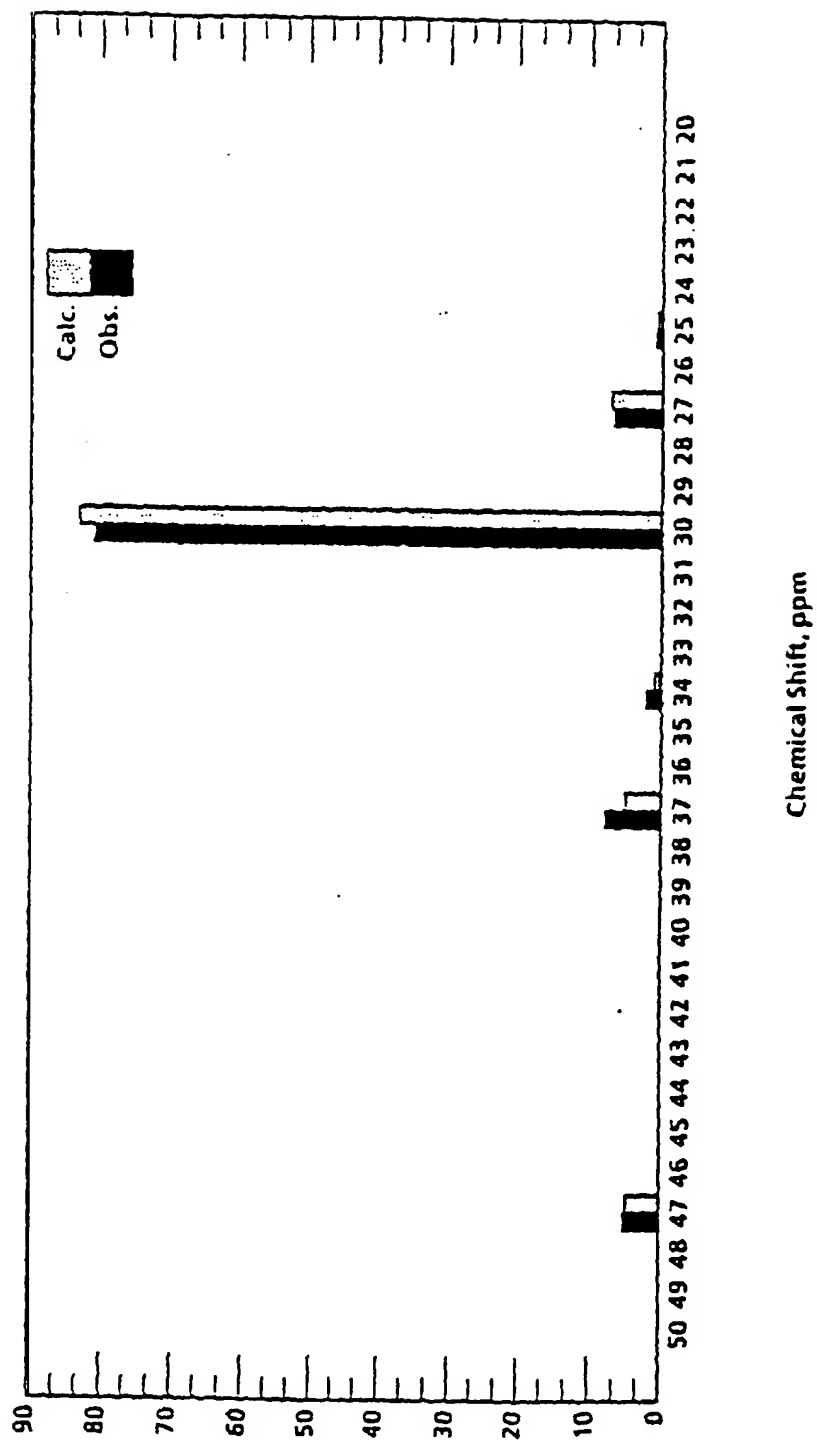


FIG. 7

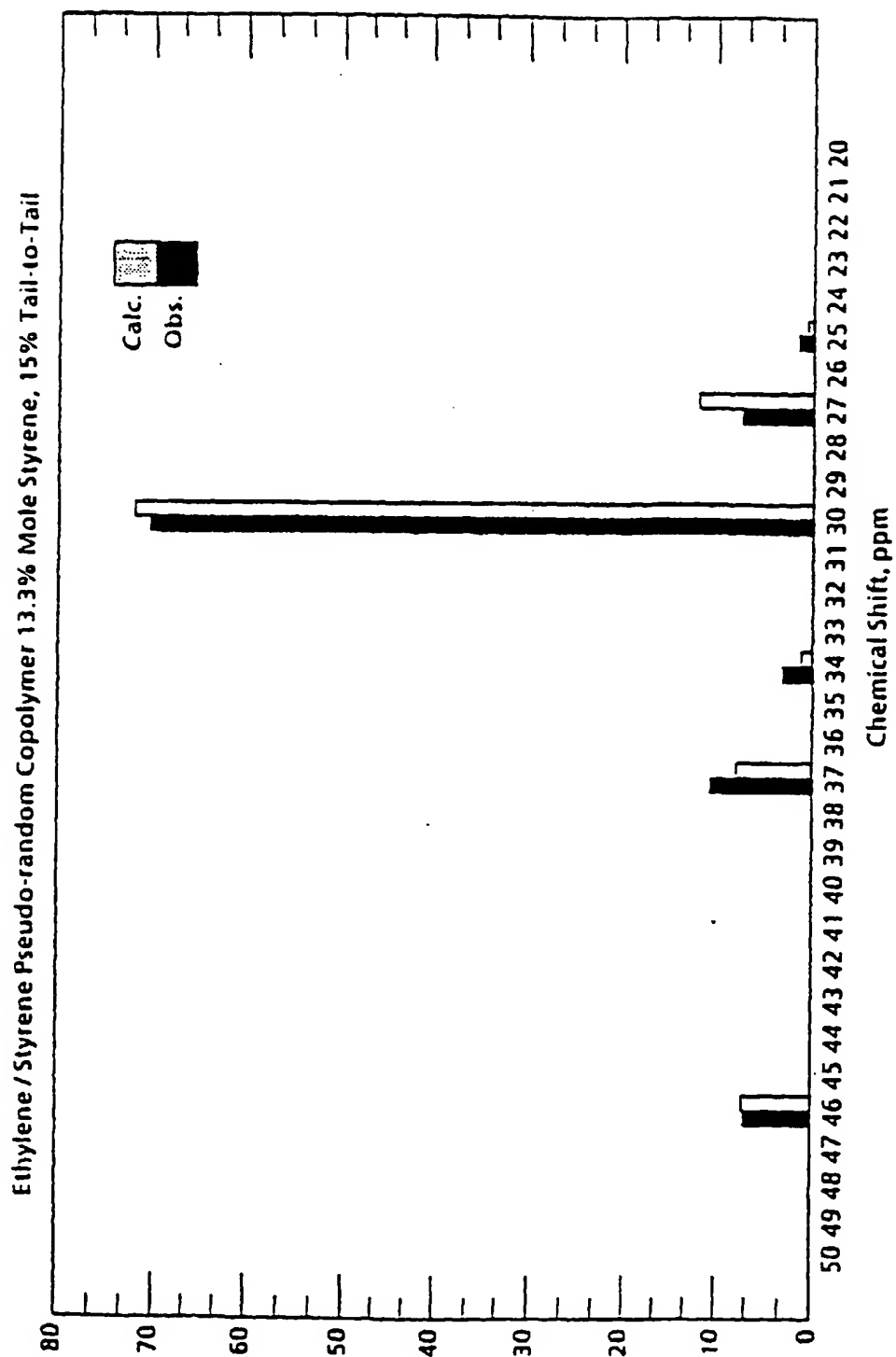


FIG. 8

Ethylene / Styrene Pseudo-random Copolymer 37 Mole % Styrene, 15% Tail-to-Tail

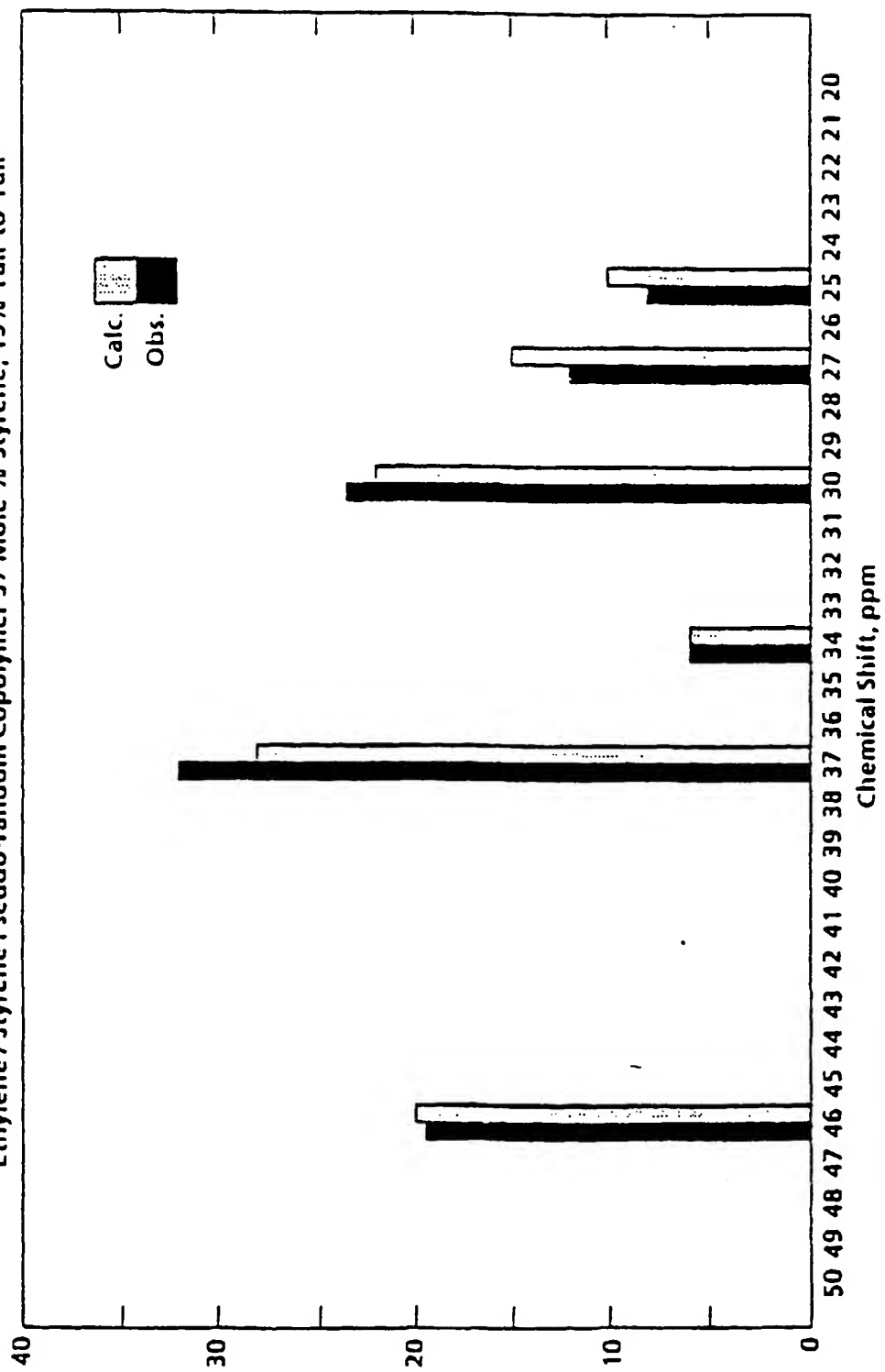
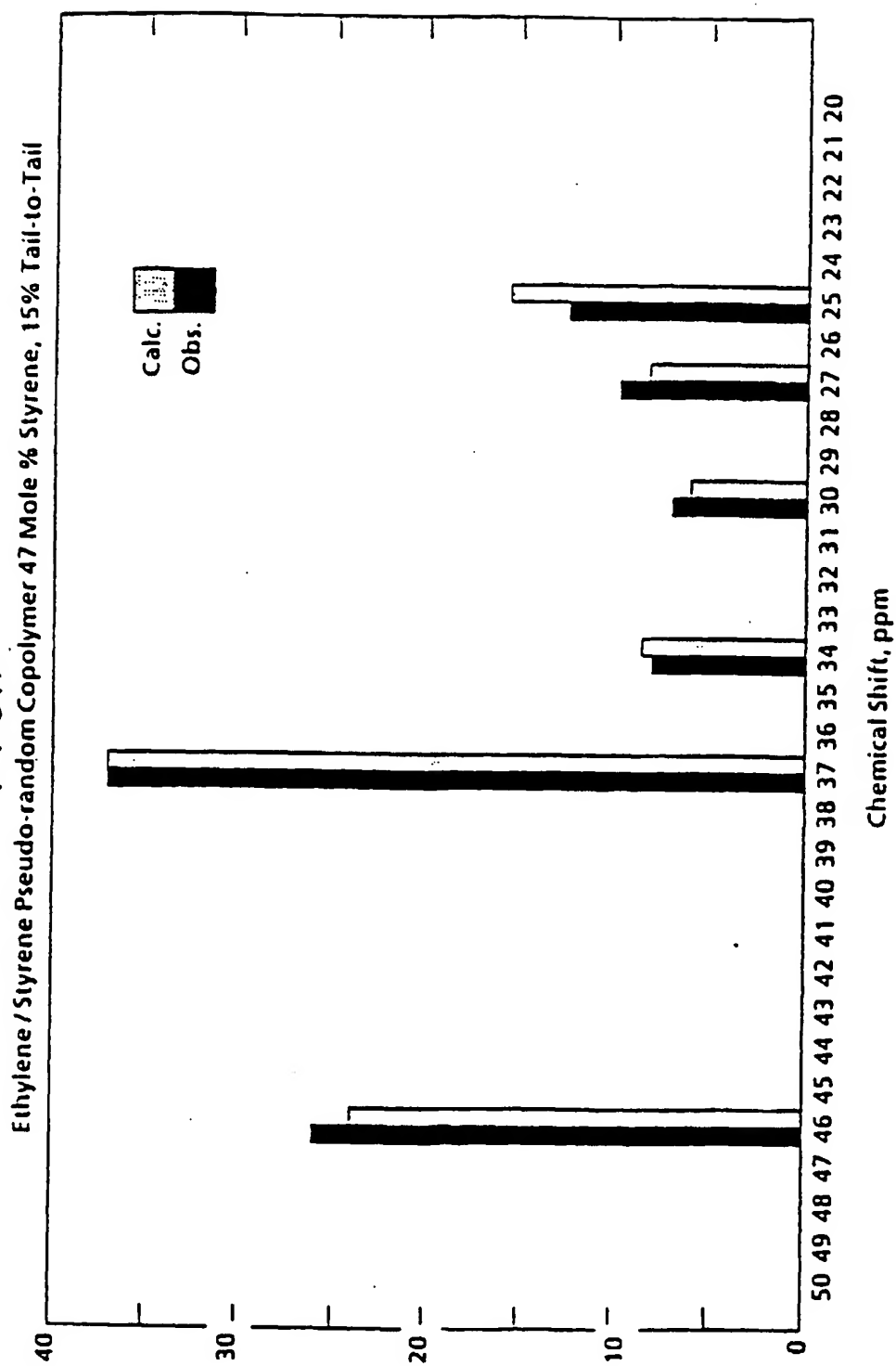
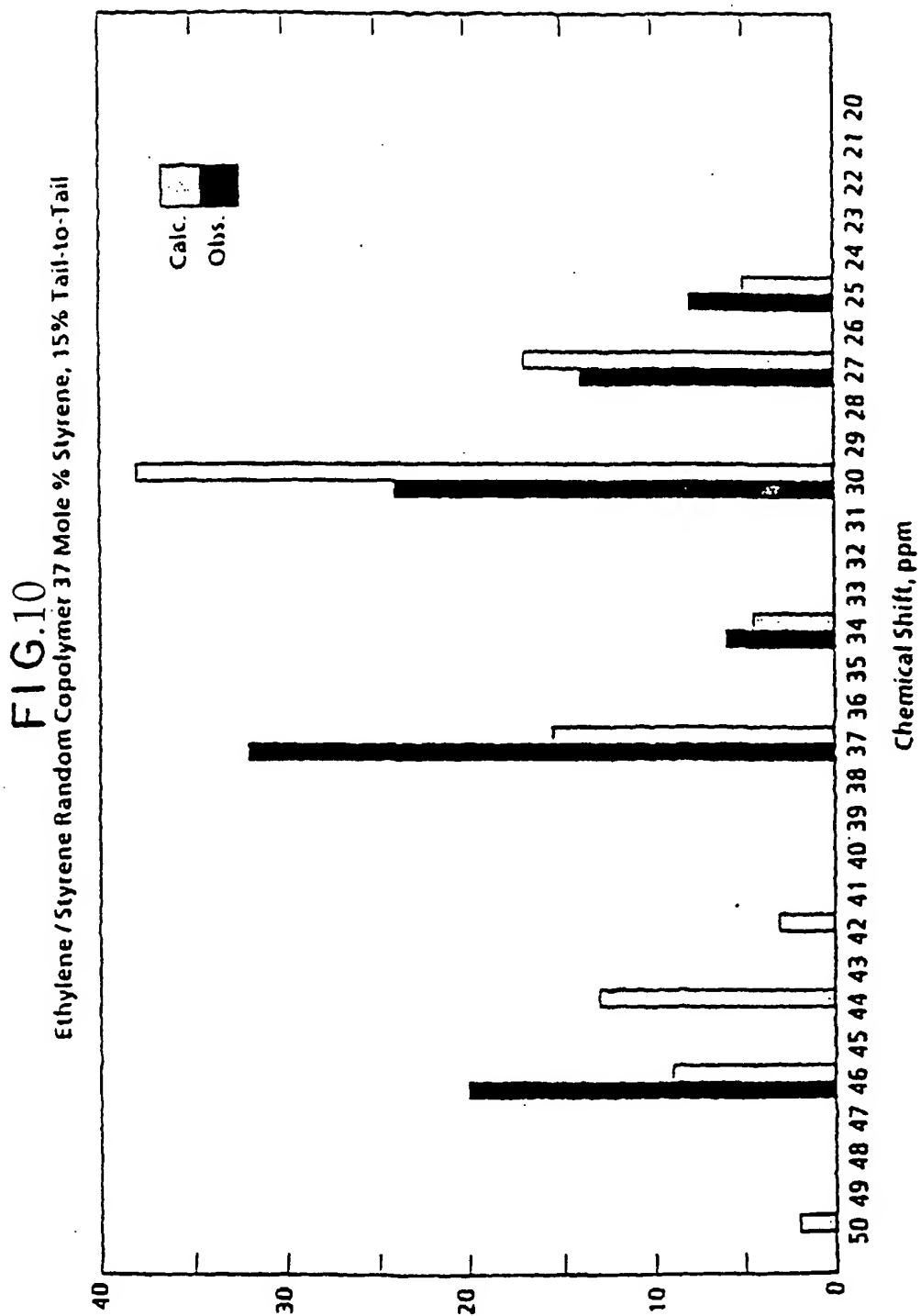


FIG. 9





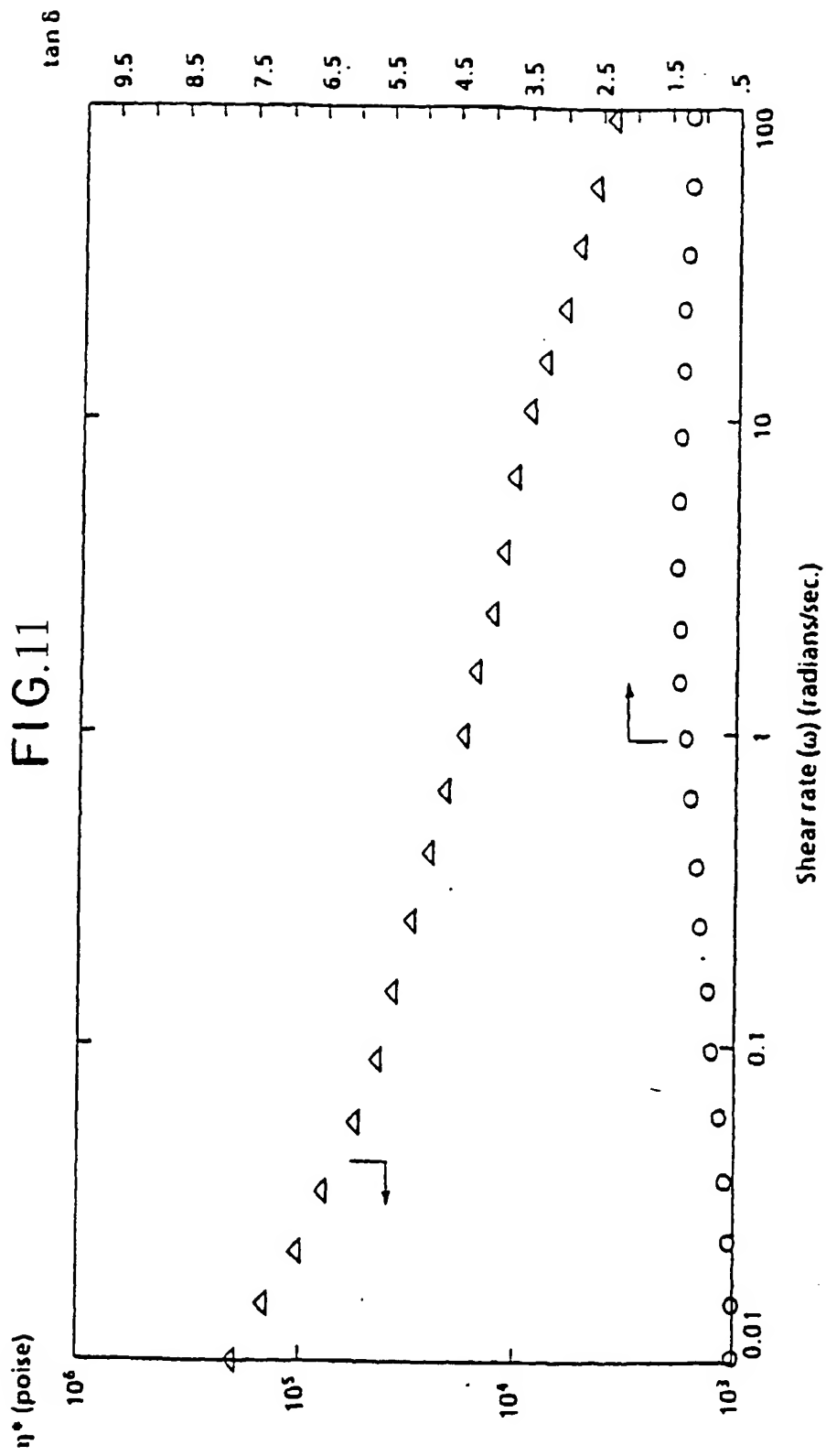
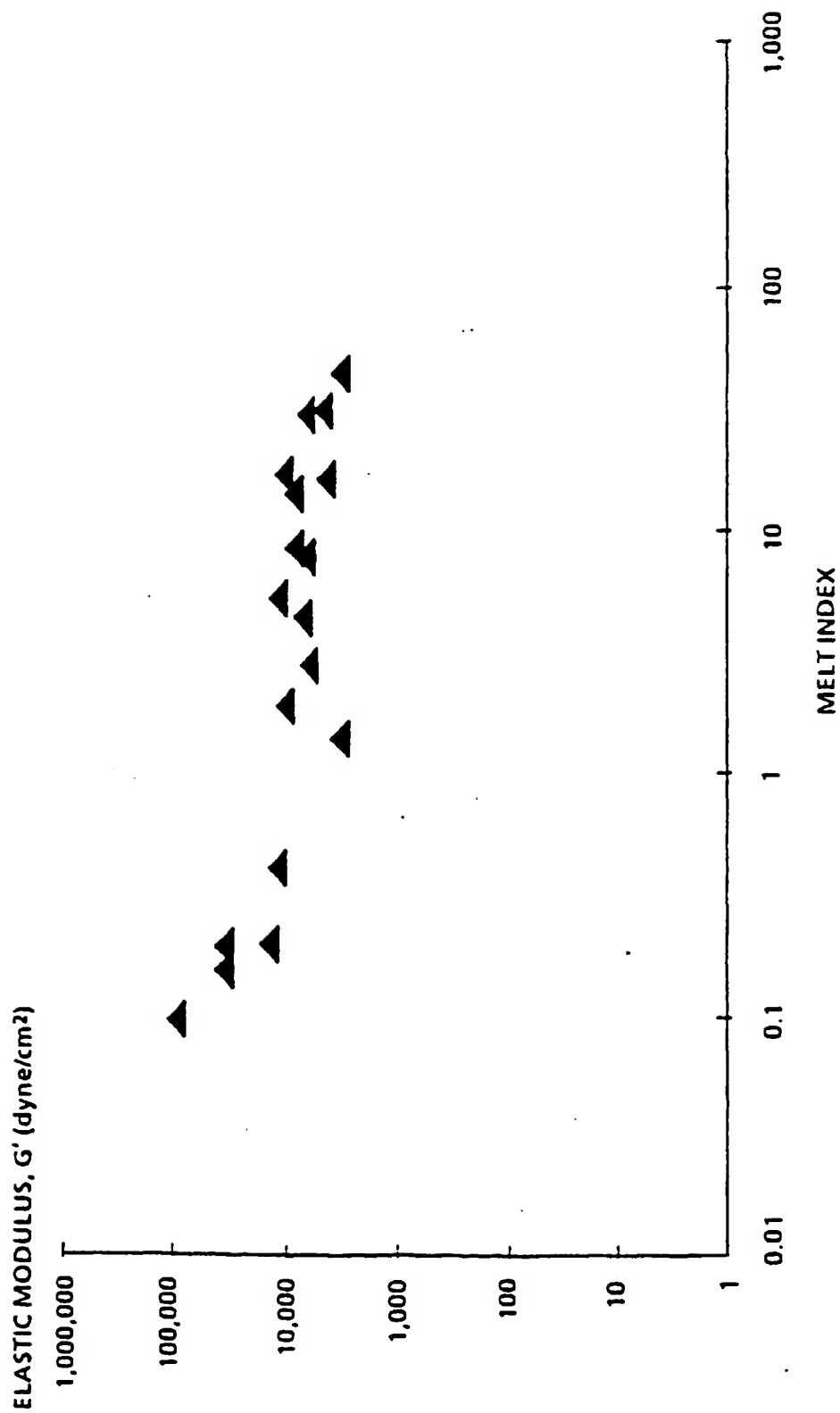
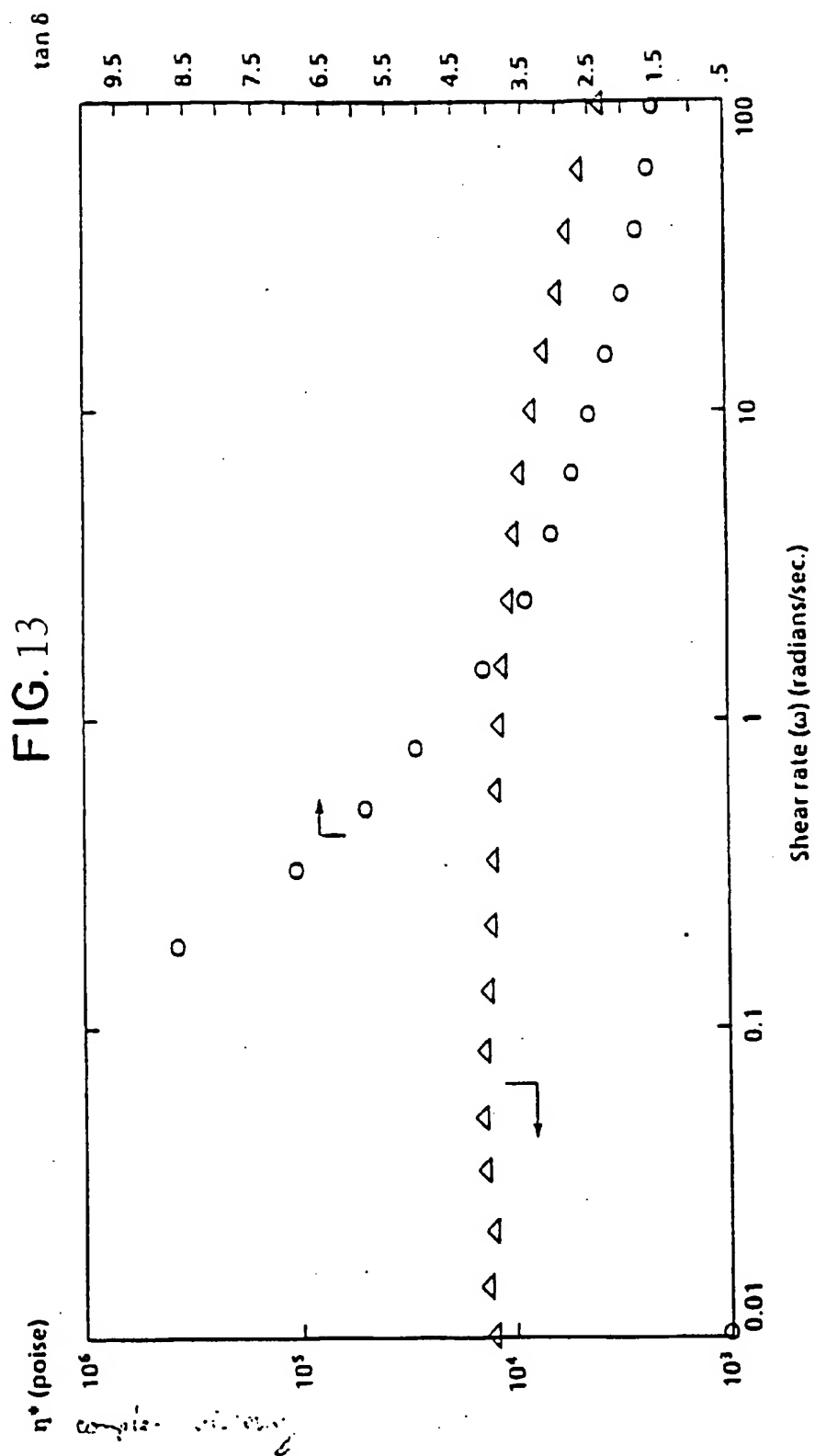


FIG.12
ELASTIC MODULUS V. MELT INDEX





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